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BY P. W. BRIDGMAN.

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(Continued from page 3 of cover.)

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2. BRIDGMAN, P. W.—Compressibilities and Pressure Coefficients of Resistance of Elements, Compounds, and Alloys, Many of Them Anomalous. pp. 27–93. March, 1933. $1.20.

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Introduction.

This paper represents the accumulation of a year and a half or two years' measurements of compressibility and pressure coefficient of resistance by methods already extensively used and described.[1]

The particular feature of this work is the discovery of a number of highly anomalous effects. Some of the anomalies are large scale and striking, as in the case of Ag_2O, already published elsewhere,[2] or of the element chromium. But most of the anomalies are small scale in character, and demand careful use of the apparatus in order to be sure that they exist. In fact some of these effects might previously have escaped notice, and have been dismissed as merely due to accidental irregularities. My assistant, Mr. L. H. Abbot, has developed a great deal of skill in the use of the lever piezometer, and has furthermore had the patience to make the large number of closely spaced readings necessary to decide whether an irregularity in the data is due to a real anomaly characteristic of the substance, or is only accidental. Every precaution has been taken to be sure that these anomalies are real and not in the apparatus. The apparatus itself has been carefully studied and recalibrated. The fact that all the readings of compressibility given in the following have been obtained with the same apparatus, and the fact that anomalies of different substances are so entirely different in character is itself guarantee of the genuineness of the effects. The explanation of the effects is not yet obvious; there is no reason to think that a single type of explanation will apply to all the phenomena. It is to be remarked that similar anomalies are beginning to appear in many places, the anomalies of NH_4Cl first discovered by Simon[3] being perhaps the best known. Whatever the explanation, a new field is here opening before us, just on the threshold of the last decimal place, which will occupy us experimentally for a long time.

Detailed Data.

Elements.

Columbium. This material was obtained from the Fansteel Co. of Chicago, and was a product of their Research Department. The measurements were made in 1929, and have been waiting since for a suitable opportunity for publication. The compressibility sample was in the form of a rod 2.6 cm. long and 3 mm. in diameter. The compressibility measurements were made as usual at 30° and 75° without incident. At 30° the average arithmetical deviation from a straight line of a single one of the 11 readings was 0.13% of the total effect, and at 75° the corresponding figure was 0.25%. The results follow:

$$\text{At } 30°, \quad -\Delta V/V_0 = 5.700 \times 10^{-7} p - 2.22 \times 10^{-12} p^2,$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 5.778 \times 10^{-7} p - 2.12 \times 10^{-12} p^2, \quad p \text{ in kg/cm}^2.$$

It is thus slightly less compressible than iron.

The resistance specimen was in the form of wire 10 cm. long and 0.050 cm. in diameter. The resistance under pressure was measured on the potentiometer, employing four terminals in the conventional way, the connections being made by spot welding. The specific resistance at 30° was 23.3×10^{-6} ohms per cm^3., somewhat high for a metal of this character. The average temperature coefficient of resistance between 0° and 100°, obtained by linear extrapolation of the readings at 30° and 75° was 0.00228. This is considerably lower than is to be expected for a pure metal, and is probable indication of not very high purity. The effect of impurity is known in practically all cases to be greater on the electrical properties than on the compressibility. The effect of pressure on resistance was measured at 30° and 75°. At each temperature the resistance is sensibly linear; at 30° the average arithmetical deviation of a single one of the 11 readings from a straight line was 0.10%, and at 75° the corresponding figure for the same number of readings was 0.27% of the maximum effect. The coefficients found were as follows:

At 30°, average coefficient 0–10000 kg, -1.21×10^{-6},

At 75°, average coefficient 0–10000 kg, -1.25×10^{-6}.

The coefficient is thus normal in sign and close in numerical value to that of cobalt, which also has about the same compressibility. Columbium thus appears to be an unexciting, prosaic substance.

Rhodium. Measurements had been made previously on this material;[4] the point in repeating them was that I had now obtained material of considerably higher purity from Johnson Matthey and Co. of London.

The compressibility measurements were made on a rod 2.5 cm. long and 2 mm. in diameter. The measurements went without incident, at 30° and 75° as usual. At 30° the average arithmetical departure from a straight line of a single one of the 17 readings was 2.9% of the maximum effect, and at 75° the corresponding figure for 14 readings was 0.7%. The results are:

$$\text{At } 30°, \quad -\Delta V/V_0 = 3.606 \times 10^{-7}p - 2.73 \times 10^{-12}p^2,$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 3.702 \times 10^{-7}p - 2.75 \times 10^{-12}p^2.$$

The thermal expansion was measured in a specially constructed apparatus used previously in measuring the expansion of single crystals. The apparatus is described in my paper dealing with single

crystals.[5] The mean linear differential expansion between Rh and Fe in the temperature range between 12° and 30° was found to be 3.49×10^{-6}, which, assuming 12.0×10^{-6} for Fe, gives 8.5×10^{-6} for Rh. International Critical Tables (I. C. T.) gives 8.4×10^{-6}.

The electrical resistance was measured on a swaged wire about 10 cm. long and 0.08 cm. in diameter. The potentiometer method with four terminals was used, the terminals being attached with soft solder. Two runs were made at 30°, agreeing within the limits of error, and a single run at 75°. At each temperature the relation between pressure and resistance was sensibly linear. The results were:

At 30°, average coefficient between 0 and 12000 kg,
$$-1.764 \times 10^{-6},$$

At 75°, average coefficient between 0 and 12000 kg,
$$-1.708 \times 10^{-6}.$$

The specific resistance, measured at 30°, was 4.95×10^{-6}, which, corrected by the temperature coefficient, gives 4.35×10^{-6} at 0° C. I. C. T. gives 4.69.

The average temperature coefficient of resistance between 0° and 100°, obtained by linear extrapolation of measurements at 30° and 75° was 0.00462. This is much higher than my previous value, 0.00399, and is evidence of the much higher purity of this material; the same is also shown by the low specific resistance.

The previous relation between pressure and resistance at 30° was: $\Delta R/R_0 = -1.738 \times 10^{-6}p + 9.7 \times 10^{-12}p^2$, which gives for the average coefficient between 0 and 12000 -1.62×10^{-6}, against -1.76 above. The difference is in the direction always found without exception to be the effect of impurity. The compressibility of the former sample at 30°, however, was: $-\Delta V/V_0 = 3.72 \times 10^{-7}p - 2.67 \times 10^{-12}p^2$, somewhat higher than the value found for this new specimen. This is somewhat unusual, but there is no universal rule here as for the resistance. It would indicate an impurity of higher compressibility in the previous sample, such, for example, as Pd.

Ruthenium. This has not been previously measured. It belongs to the hexagonal system, so that the following results can only be a mean of some sort for different directions. The material was obtained from Johnson and Matthey at the same time as the rhodium. The compressibility specimen was in the form of a swaged rod 2.7 cm. long and 3 mm. in diameter. It was not perfectly regular in appear-

ance, but appeared as if there might be seams in it. On the first application of pressure there was a large change of zero. This may have been due to seams, or to the fact that the crystal system is not cubic; large effects of this nature are to be expected for non-cubic materials. Two more applications of 12000 were made before the routine measurements were attempted. Also at 75° an additional seasoning application of 12000 was made before the measurements. This seasoning seemed effective, for the change of zero during the measurements, both at 30° and 75°, was not more than the irregularity of the other points. At 30° the average arithmetical departure from a straight line of a single one of the 13 readings (after making one discard) was 1.3% of the maximum effect, and at 75° the corresponding figure for 15 readings was 0.64%. As in the case of Rh, the relative irregularity is greater than usual because of the smallness of the compressibility; the absolute irregularity is not greater, and in fact is even less than usual. There may be some significance in the fact that the discarded point at 30° was at the maximum pressure. This was off the curve by one third of the total effect; there is perhaps a possibility that this is a genuine anomaly like that of many of the other substances of this paper, but it would have been very difficult to establish, because it was at the end of the pressure range, and the matter was not investigated further.

The results for volume compressibility, assuming equal linear compressibility in all directions, are:

$$\text{At } 30°, \quad -\Delta V/V_0 = 3.42 \times 10^{-7} p - 2.13 \times 10^{-12} p^2,$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 3.45 \times 10^{-7} p - 2.13 \times 10^{-12} p^2.$$

The average compressibility is therefore slightly less than that of Rh, and fits in with what might be expected from the periodic table.

The linear thermal expansion at atmospheric pressure was measured in the same special apparatus as used for Rh. The mean value between 32° and 13° was 6.75×10^{-6}. I. C. T. gives 9.1; this very marked divergence is perhaps to be ascribed to the non-cubic symmetry of the crystal, for it is now pretty well established that measurements by different observers on different specimens of non-cubic metals are likely to give different results. The principal value of such measurements on multi-crystalline aggregates is in establishing upper and lower limits for the constants corresponding to different directions in the crystal.

The resistance was measured on the compressibility sample, the technical difficulties having proved too great to permit swaging it to

a more slender rod, as had been possible with Rh. The current was led in through copper terminals making soldered connection over the entire flat ends. In this way the lines of current flow are straight from the beginning, and end effects are avoided. The current, about one half amp., was made as large as possible without introducing troublesome thermal effects. It was supplied from a storage battery, through heavy manganin resistances in an oil bath. The resistance was very low, only 0.00022 ohms, so that the measurements could not be as accurate as usual, in spite of the large current. Pressure measurements were made at 0° and 95°. Within the limits of error the relation between pressure and resistance was linear. At 0°, the average arithmetical departure of a single one of the 16 readings from a straight line was 2.2% of the pressure effect, and the corresponding figure at 95° for 13 readings was also 2.2%. The results were:

At 0°, average coefficient 0–12000, -2.48×10^{-6},

At 95°, average coefficient 0–12000, -3.20×10^{-6}.

So large an effect of temperature is not usual.

Other electrical data were also obtained. At 0° the specific resistance is 7.64×10^{-6}. I. C. T. gives 10×10^{-6}, to only one significant figure. The temperature coefficient of resistance at atmospheric pressure was determined from readings at 0°, 24° 50°, and 95°. The relation between resistance and temperature is of the second degree in the temperature, namely:

$$R = R_0 [1 + .00494t - 3.64 \times 10^{-6} t^2].$$

The negative sign for the second term is not usual for most metals, but seems to be of frequent occurrence in the metals of the platinum groups. This formula gives for the average coefficient between 0° and 100° 0.00458. There seems to be no previous value for comparison, but this is high for a metal of this character, considerably higher than for pure platinum, for example, and is in so far evidence of high purity.

Chromium. The compressibility of this element has been previously measured,[6] but the purity was not high, and repetition was desirable. The previous sample was highly brittle, and in appearance was like the metal which has been available for many years made by the Goldschmidt process. Its compressibility was not notable in any way, being 5.19×10^{-7} at 30°, somewhat less than for Fe. For the new measurements I was fortunate to obtain from Mr. P. H. Brace of

the Research Department of the Westinghouse Electric and Manufacturing Co. a swaged rod of Cr. Mechanically, this was soft enough to be readily filed; the hardness of commercial chromium plating is said to be due to occluded hydrogen. This specimen had been made in connection with a systematic study of the properties of the pure metal, and every effort had been made to obtain metal of high purity; the fact that it was malleable enough to be swaged is evidence that it was much purer than the previous sample. In order to further test the purity, Dr. Martin Grabau was kind enough to make a spectroscopic examination under the direction of Professor F. A. Saunders, and it was found to be of quite an exceptional degree of purity, the only detected impurity being a doubtful trace of magnesium.

Only one piece of this chromium was available, a rod 4 cm. long and 2.5 mm. in diameter. The resistance was first measured, and then the length of the rod was cut to 2.7 cm. for the compressibility measurements. The resistance measurements suggested most unusual compressibility effects, which were indeed found. Readings of compressibility were made at the usual 30° and 75°, and also at − 40°, since the resistance measurements had suggested the possibility of new effects at low temperatures. The temperature bath at − 40° consisted of about 5 gallons of alcohol, rapidly stirred, into which small pieces of solid CO_2 were dropped when required to maintain the temperature constant as indicated on a pentane thermometer. The regulation was done by hand, one observer continually watching the temperature bath, while the other made the compressibility readings. The results were highly unusual, as shown in Figure 1. In this figure the actual displacements of the slider of the potentiometer are recorded, multiplied by such a constant as to reduce them approximately to changes of length relative to the steel of which the piezometer is made. At 30° and 75° Cr is on the average less compressible than Fe, but the difference is far from linear, and behaves in the complicated way shown. Except for one point which may have involved a blunder in reading, although this is not likely, all the points at these two temperatures lie close to a single curve, that is, there is no difference between increasing and decreasing pressure. In fact, the direction of alteration of pressure was changed several times in order to be sure that the curve is really characteristic of the metal, and does not involve its past history. At − 40°, on the other hand, the character of the phenomena is entirely altered; the compressibility is now greater than that of Fe, the sinuosities in the curve of change of

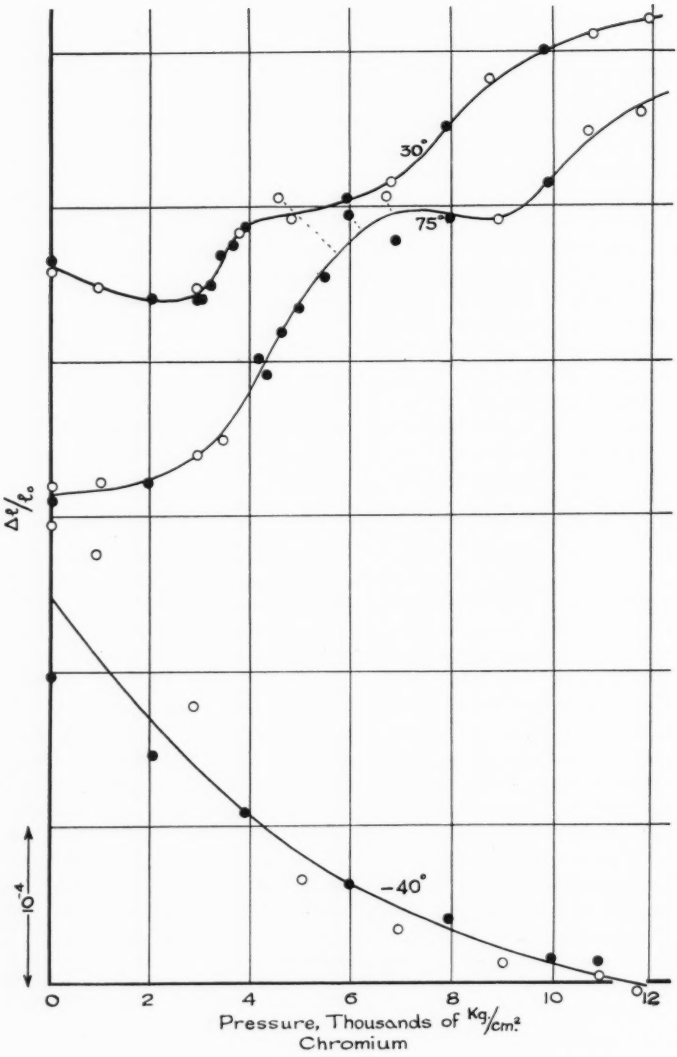

FIGURE 1. Deviations from linearity of the linear compression of chromium. The open circles are for increasing pressure and the solid circles for decreasing pressure.

length have now disappeared, and there is a distinct hysteresis between the readings with increasing and decreasing pressure. It is possible that the hysteresis would have disappeared if the pressure run had been repeated, but because of the inconvenience of maintaining temperature at − 40°, this was not attempted, but the mean result, indicated by the curve, was used in the final calculations. The final results for change of volume are shown in Table I. Chromium is cubic, so that the volume changes can be accurately computed from the changes of length in a single direction. In making the calculations at − 40° the compressibility of iron was extrapolated linearly from the measured values at 30° and 75°.

TABLE I.

RELATIVE VOLUME CHANGES OF CHROMIUM.

Pressure kg/cm²	$\Delta V/V_0$		
	− 40°	+ 30°	+ 75°
1000		000606	000552
2000	.001320	001167	001089
3000		1611	1605
4000	2577	2109	2049
5000		2622	2430
6000	3717	3129	2826
7000		3618	3336
8000	4869	4044	3876
9000		4473	4410
10000	5940	4938	4878
11000		5427	5310
12000	6981	5910	5772

The resistance was measured, as already stated, on the same rod as that from which the compressibility sample was cut. It proved not to be possible to soft solder this, and spot welding on so large a diameter was not practical with the equipment on hand. Current connections at the two ends were made by massive sleeves of copper driven tightly over the ends. Under pressure these become even tighter because of differential compressibility. The design of the current connections is thus such as to start the lines of current flow approximately straight, avoiding end effects. The potential terminals were fine springs. It was soon found that the behavior of resistance is so complicated as to make it desirable to extend the study of resistance over a wider temperature range than usual. In addition

to the conventional measurements at 30° and 75°, runs were also made at 0°, − 20°, − 40°, and − 78.5°, the latter being the normal sublimation point of solid CO_2. The temperatures below 0° were obtained in an alcohol bath, cooled with solid CO_2 and regulated manually by a second observer, as already explained. The greatest difficulty to be anticipated at low temperatures is the freezing of the pressure transmitting liquid. Of all the substances liquid under ordinary

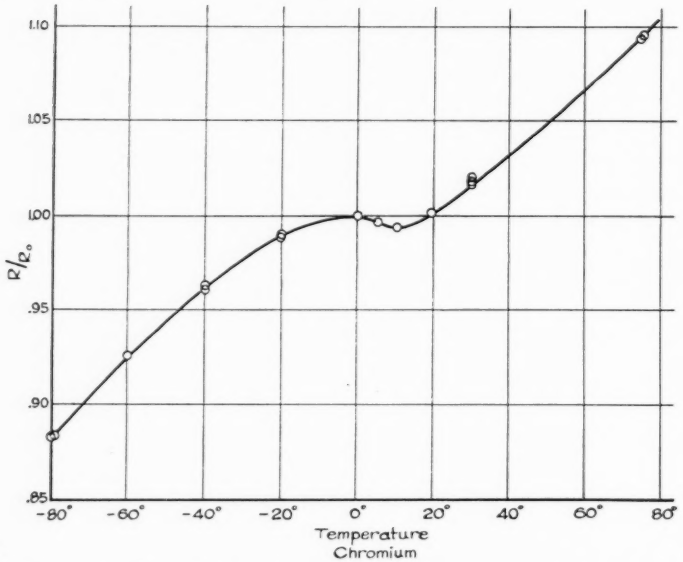

FIGURE 2. The relative resistance of chromium at atmospheric pressure as a function of temperature.

atmospheric conditions, and therefore capable of being used without the introduction of complicated precompressors, as would be necessary in handling a gas, iso-pentane is that with the lowest freezing point, and this was accordingly tried. It proved gratifyingly successful. It allowed readings at − 78.5° to a maximum pressure of 8000 kg/cm² before its viscosity became too great (or before it froze, which, was not determined), and at − 40° and higher, readings to the full 12000.

Not only is the resistance abnormal when measured as a function of pressure at constant temperature, but it is also abnormal at atmospheric pressure as a function of temperature, an effect apparently not observed before because pure enough metal was not available. At 0° at atmospheric pressure the specific resistance is 18.9×10^{-6}. The only figure given by I. C. T. is 2.6 for the pure metal on the authority of Shukov. This cannot possibly be correct, but would indicate a misprint somewhere. The relative resistance as a function of temperature at atmospheric pressure is reproduced in Figure 2. The curve is very similar in character to the curve for the volume of liquid water, with an abnormality in the neighborhood of 0° C. of much the same kind. It is to be noticed that there is no hysteresis between resistance and temperature, but within the limits of error the relation is single valued. The order of the readings was as follows: first, 3 points at 30°, made before and after the pressure run, then at 75°, 30° again, 0°, − 78.5°, − 60°, − 40°, − 20°, + 20°, + 30°, + 10°, and + 5°.

The relative resistance as a function of pressure is reproduced in Figure 3, where all the experimental points are shown. The scale of the figure is not large enough to show any departure of these points from smooth curves. In practically all cases the points alternated between increasing and decreasing pressure, readings being made on the odd thousands with increasing pressure, and on the even thousands with decreasing pressure. There is no appreciable hysteresis, even at − 40°, although the compressibility measurements, made after the resistance measurements, did show hysteresis. The crossing of the curves means that there are regions, varying with the pressure, in which the temperature coefficient of resistance is negative. This, of course, is to be expected because such a phenomenon has already been found at atmospheric pressure.

The curves for the resistance and the compressibility must speak for themselves, and I shall not attempt to make any comment except to emphasize that whatever internal change it is which is responsible for the anomalies occurs for the most part without hysteresis, and to remark that manganese, which occurs next to chromium in the periodic table, is known to have polymorphic transitions at atmospheric pressure and to have a highly complicated crystal structure with 54 atoms in the unit cell. It is also to be noted that internal changes like these of pure chromium may be suppressed by impurities, the previous measurements of compressibility having given no hint of the complications now found.

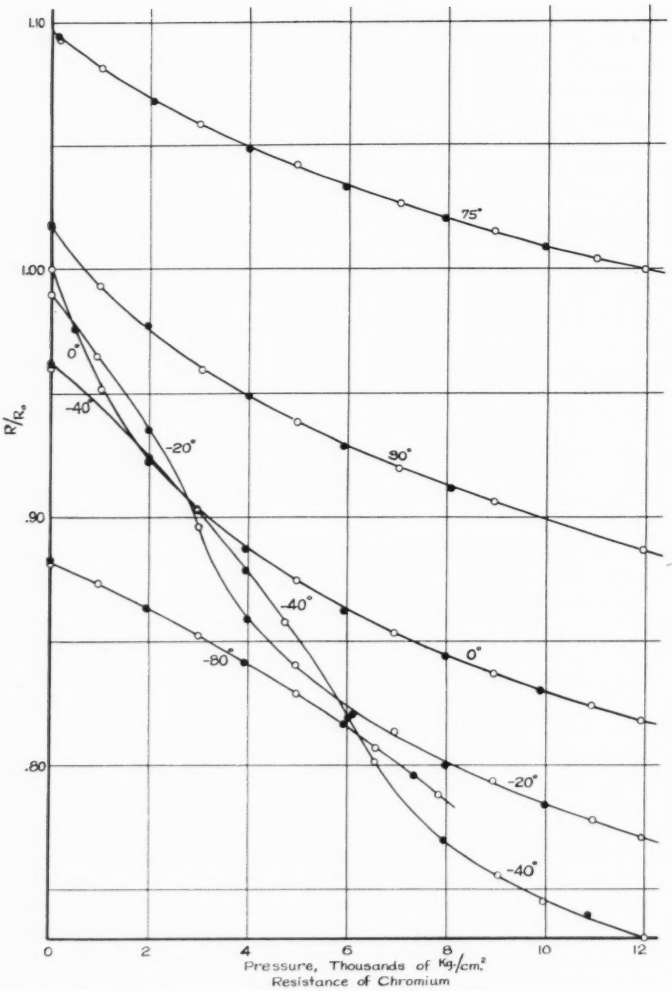

FIGURE 3. The relative resistance of chromium as a function of pressure at various temperatures. The open circles are for increasing pressure and the solid circles for decreasing pressure.

Arsenic. Measurements have already been made of polycrystalline arsenic on two different occasions.[7] The second measurements were made on samples which were approximately single grains, in that there was a strongly preferred direction of orientation. Surprising results were found; it appeared that there must be a polymorphic transition in the neighborhood of 5500 kg., and it was evident that there were very large differences in different directions. However, the results were not consistent, and in particular there were obscure effects on the first application of pressure for which no parallel in the behavior of other substances was known. It seemed evident that satisfactory results could not be expected until truly single crystals were available.

Measurements have now been made on a number of single crystals, without even yet, however, leading to a completely satisfactory cleaning up of the situation. The preparation of single crystals proved an unexpectedly complicated and difficult matter, and Dr. W. E. Danforth, as my assistant, spent a good part of an academic year working out the technique and producing the crystals. The original material was of the "Kahlbaum" grade. This proved to have a very appreciable fraction of non-volatile impurity, probably carbon or silicon. The metal was first purified by a vacuum distillation in pyrex at 500° C, removing the non-volatile impurities, and also separating out the volatile As_2O_3, the metallic arsenic condensing in the intermediate part of the tube. The final crystallization was in heavy quartz tubes. The powdered arsenic from the first purification was introduced into a bulb at one end of the tube, which was bent into several straight lengths to give different orientations in the final crystal. During the exposure to the atmosphere incident to getting into the quartz, more As_2O_3 was formed, which had to be eliminated by a second distillation. This second distillation was at 300°, which drove the As_2O_3 into an end of the tube left projecting from the furnace. This end was then sealed off from the rest of the tube, thus removing the As_2O_3. The quartz was then lowered at about 30 cm. per hour from a furnace maintained at 950°, well above the triple point temperature. The pressure at the triple point is 36 atmospheres. The quartz is amply strong to hold this pressure if perfect seals are made. The casting obtained after lowering out of the furnace was expected to be a single grain, but experience proved that it usually was not. Accordingly, after the first lowering from the furnace the now empty bulb was sealed off, leaving merely the bent tube fairly well filled with arsenic. This was now run through the furnace again in the opposite direction, and this second crystallization usually produced a single grain.

There is a very strong tendency for the principal hexagonal axis to lie in a horizontal plane (cleavage plane vertical), and in fact this proved to be practically invariable, so that the only way of getting other orientations was to bend the tube. Successful specimens of high orientations are extremely difficult to get, however, because the thermal contraction across the cleavage planes is so high that if the cleavage plane makes much of an angle with the length the rod will break spontaneously into short pieces a few mm. long on cooling. The highest orientation that was obtained was 50° between cleavage plane and length, and this was exceptional, angles greater than 10° being rare.

Crystals were made in two sizes: 3 mm. in diameter for measurements of compressibility and about 1 mm. for measurements of resistance. Resistance measurements were made on two samples of 90° between axis and length (cleavage plane parallel to length), one of 83°, and one of 73°. Compressibility measurements were made on two 90° orientations, one 79°, one 56.5°, and one 40°. The results were highly abnormal; it is difficult to decide just how much should be reproduced here, since the abnormalities are in some respects not reproducible. In general characterization, it appears that the direction perpendicular to the axis, in the cleavage plane, is abnormal, but along the axis, the behavior is quite smooth and canonical. One might at first be inclined to expect the opposite behavior, looking perhaps for irregularities associated with the closing together of the atoms in the direction of greatest separation, that is, across the cleavage plane. That the abnormalities are in the opposite direction indicates interpenetration effects in the direction of closest packing, the fields of force being more symmetrical at larger distances of atomic separation. The crystal arrangement of arsenic is much like that of bismuth and antimony, which are also abnormal in many particulars, but not to as extreme a degree as arsenic. One may suspect an unusual asymmetry in the arsenic atom.

The two compressibility measurements on the two 90° orientations agreed in showing several ranges of pressure in which the change of length is approximately a linear function of pressure, the different ranges running into each other continuously with a break only in the derivative, so that there is no evidence for a polymorphic transition of the ordinary kind, as was suspected from the previous measurements. But on the other hand, there is no exact correspondence between the results for the different samples. The first sample showed at 30° linear ranges from 0 to 4060, from 4060 to 6300, and from 6300

to 12000 kg/cm². This specimen showed no hysteresis at all on the very first application of pressure. Similarly at 75°, there were three ranges, from 0 to 3400, from 3400 to 7600, and from 7600 to 12000, and there was also no hysteresis except at the two lowest points, 700 kg. and atmospheric pressure. The second 90° orientation, on the other hand, showed at 30° on the first application of pressure very

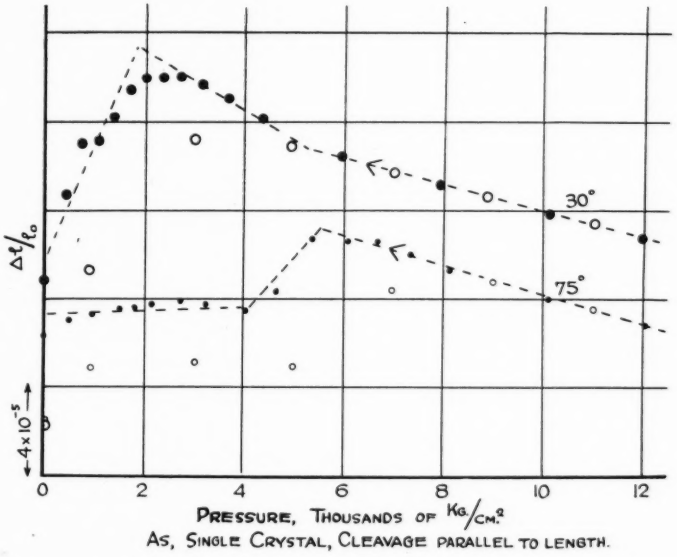

FIGURE 4. Differential linear compression of single crystal arsenic, cleavage plane parallel to length. The larger circles are for 30° and the smaller for 75°; open circles with increasing pressure, and solid circles with decreasing pressure.

marked hysteresis up to 5200, but from here on the same perfectly linear hebavior up to 12000. Similarly at 75°, there was hysteresis, this time up to 8000, but from here on linear behavior. The low pressure episodes on this second sample were not linear like those of the first; they are reproduced in figure 4. The straight lines indicated in this figure are obviously only a rough approximation, but they are sufficiently good considering the failure of reproducibility, and it is

the results given by the straight lines which are reproduced below. The 79° orientation gave essentially a linear relation at both temperatures over the entire pressure range, except for slight curvature at the low pressure end. There was, however, marked hysteresis at 30°. The 56.5° orientation gave results of considerable irregularity,

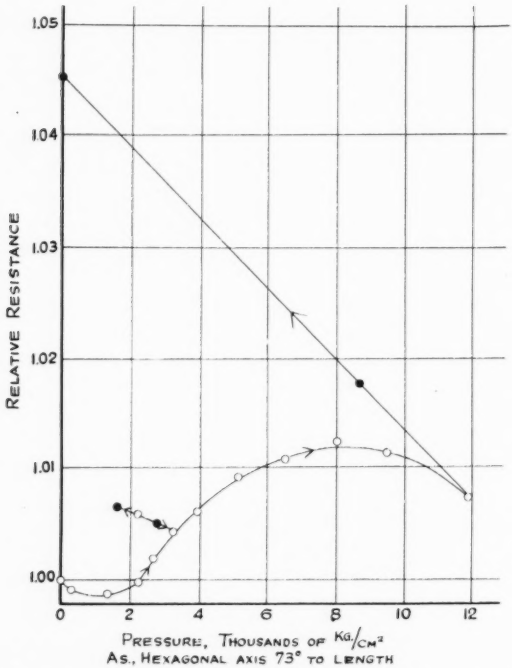

FIGURE 5. The relative resistance at 30° C of single crystal arsenic, hexagonal axis 73° to length, on the initial application of pressure.

with hysteresis. They can be fairly well reproduced by assuming at each temperature two linear ranges; at 30° from 0 to 7100 and from 7100 to 12000, and at 75° from 0 to 4800 and from 4800 to 12000. It is not certain, however, whether these effects are legitimate, because of difficulties in the preparation of the specimen. Two pieces of this orientation were used, each only 2.3 mm. long, piled together with

three steel separators to make up the length required by the piezometer. The ends were not perfectly flat, and the irregular effects may have been geometrical, due to rocking of one piece on another. The linear results are reproduced below, but the average compressibility, 0 to 12000, is much more secure than the results for the separate ranges. The 40° orientation gave results like those for any normal

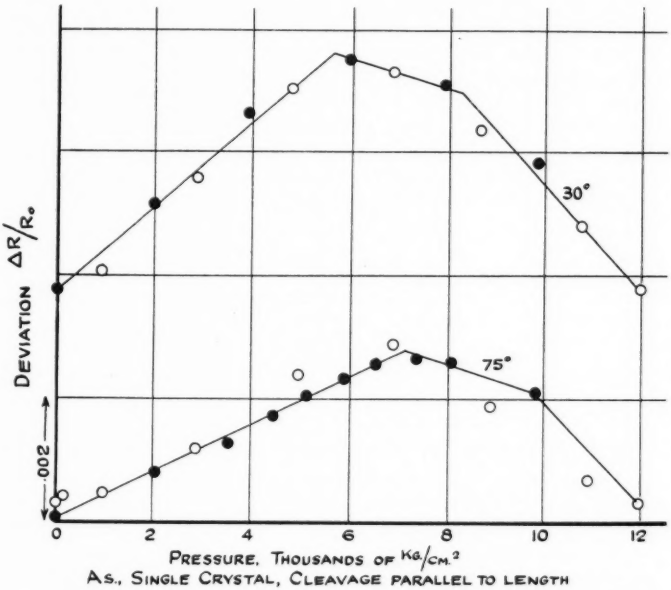

FIGURE 6. Deviation from linearity of the change of relative resistance of single crystal arsenic, hexagonal axis perpendicular to the length, at 30° and 75°. The open circles are for increasing pressure and the solid circles for decreasing pressure.

material; there was no evidence of separate episodes, the hysteresis, although perceptible, was slight, and there were no important seasoning effects on the first application of pressure. The average deviation of single points at both temperatures from smooth curves through the centers of the hysteresis loops was 0.4% of the maximum effect; the deviation would be much less if the two branches of the hysteresis loops were treated separately.

The resistance samples covered a smaller range of orientations: there were two of 90°, one of 83°, and one of 73°. The results of the resistance measurements agreed in that the whole pressure range breaks up into sub ranges, but did not agree with regard to the first seasoning effects of pressure. One 90° and the 83° orientation showed

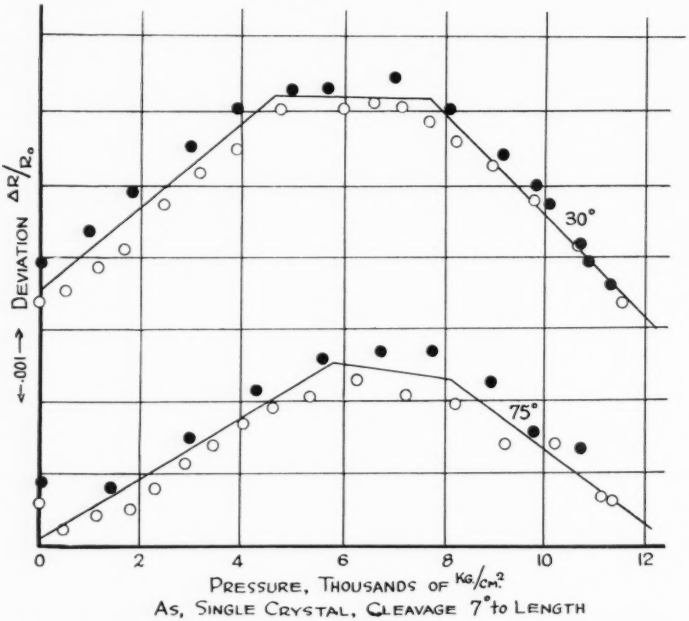

FIGURE 7. Deviation from linearity of the change of relative resistance of single crystal arsenic, hexagonal axis 83° to the length, at 30° and 75°. The open circles are for increasing pressure and the solid circles for decreasing pressure.

no seasoning effects at all, but the other two specimens showed very large seasoning effects of the same general character. The effect of the first application of pressure on the resistance of the 73° specimen is reproduced in Figure 5. It is the same sort of thing as was previously obtained with polygrained material, and accounts for the apparently positive coefficient at low pressures of the virgin specimen, followed

by a permanent negative coefficient. After the first application of pressure, there was very little hysteresis between resistance and pressure, but the behavior became steady almost at once. Unfortunately, the first 90° specimen, which showed no initial seasoning effects, did later develop irregularities, and on removing from the pressure cylinder fell apart into several pieces, so that the results had to be discarded. Within the somewhat wider limits of error, the results on it agreed with those of the other 90° orientation obtained after seasoning was complete. In figures 6 and 7 the deviations from linearity of resistance as a function of pressure for the second 90° orientation and the 83° orientation are given. It is not difficult, knowing already from the compressibility measurements that there are linear ranges, to persuade oneself that there are linear ranges here, which are indicated in the figures. It must be remembered that in general resistance has proved much less sensitive to this sort of irregularity than compressibility.

The numerical results now follow.

Compressibility.

First 90° orientation.

30°

$$0\text{–}\ 4050, -\Delta l/l_0 = -\ 1.46 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$
$$4050\text{–}\ 6300, -\Delta l/l_0 = \quad 1.76 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$
$$6300\text{–}12000, -\Delta l/l_0 = \quad 1.88 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$

Average, 0–12000, 1.850×10^{-7}

75°

$$0\text{–}\ 3400, -\Delta l/l_0 = 1.41 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$
$$3400\text{–}\ 7600, -\Delta l/l_0 = 1.69 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$
$$7600\text{–}12000, -\Delta l/l_0 = 1.94 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$

Average, 0–12000, 1.680×10^{-7}

Second 90° orientation.

30°

$$0\text{–}\ 1850, -\Delta l/l_0 = 0.43 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$
$$1850\text{–}\ 5200, -\Delta l/l_0 = 2.30 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$
$$5200\text{–}12000, -\Delta l/l_0 = 1.88 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$

Average, 0–12000, 1.786×10^{-7}

75°

$$0\text{–}\ 4300, -\Delta l/l_0 = 1.70 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$
$$4300\text{–}\ 5300, -\Delta l/l_0 = 1.12 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$
$$5300\text{–}12000, -\Delta l/l_0 = 1.90 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$

Average, 0–12000, 1.771×10^{-7}

79° orientation.

30°

$$-\Delta l/l_0 = 1.826 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$

75°

$$-\Delta l/l_0 = 1.867 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$

56°.5 orientation.

30°

$$0\text{–}\ 7100, -\Delta l/l_0 = 5.87 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$
$$7100\text{–}12000, -\Delta l/l_0 = 3.19 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$

Assuming no breaks:

$$0\text{–}12000, -\Delta l/l_0 = 4.77 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$

75°

$$0\text{–}\ 4800, -\Delta l/l_0 = 7.61 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$
$$4800\text{–}12000, -\Delta l/l_0 = 3.35 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$

Assuming no breaks:

$$0\text{–}12000, -\Delta l/l_0 = 5.04 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$$

40° orientation.

$$\text{At } 30°, -\Delta l/l_0 = 16.75 \times 10^{-7}p - 36.1 \times 10^{-12}p^2$$
$$\text{At } 75°, -\Delta l/l_0 = 17.38 \times 10^{-7}p - 37.4 \times 10^{-12}p^2$$

The figures just given for the 40° orientation are only approximate, for the relation differs markedly from the second degree. The second degree formulas are so constructed as to give the correct changes of length at 0, 6000 and 12000. At intermediate points the actual changes of length can be obtained by combining with the second degree formulas a deviation curve. These deviation curves can be drawn with sufficient accuracy from the following specifications. At 30° the change of length is greater numerically at 3000 by 0.000177 than given by the second degree formula and at 9000 0.000164 less.

At 75° the actual change of length is greater numerically at 3000 by 0.000239 than given by the formula, and at 9000 0.000164 less. The maximum deviation from linearity at each temperature comes at 4600 instead of 6000 as it would if the relation were second degree.

Resistance:

90° orientation.

Specific resistance at 30°, 27.5×10^{-6}

Average temperature coefficient, 0–100°, + 0.00479.

30°

$$0- \ 5500, \Delta R/R_0 = -1.74 \times 10^{-6} p$$
$$5500- \ 8200, \Delta R/R_0 = -2.68 \times 10^{-6} p$$
$$8200-12000, \Delta R/R_0 = -3.30 \times 10^{-6} p$$

75°

$$0- \ 7100, \Delta R/R_0 = -1.56 \times 10^{-6} p$$
$$7100- \ 9800, \Delta R/R_0 = -2.08 \times 10^{-6} p$$
$$9800-12000, \Delta R/R_0 = -2.58 \times 10^{-6} p$$

83° orientation.

Specific resistance at 30°, 27.6×10^{-6}

Average temperature coefficient, 0–100°, .00483

30°

$$0- \ 4800, \Delta R/R_0 = -1.33 \times 10^{-6} p$$
$$4800- \ 7400, \Delta R/R_0 = -1.81 \times 10^{-6} p$$
$$7400-12000, \Delta R/R_0 = -2.34 \times 10^{-6} p$$

75°

$$0- \ 6100, \Delta R/R_0 = -1.08 \times 10^{-6} p$$
$$6100- \ 8200, \Delta R/R_0 = -1.43 \times 10^{-6} p$$
$$8200-12000, \Delta R/R_0 = -1.96 \times 10^{-6} p$$

73° orientation.

Specific resistance at 30°, 30.4×10^{-6}

Average temperature coefficient, 0–100°, .00472

30°

$$0- \ 2550, \Delta R/R_0 = -2.77 \times 10^{-6} p$$
$$2550- \ 8200, \Delta R/R_0 = -2.59 \times 10^{-6} p$$
$$8200-12000, \Delta R/R_0 = -2.88 \times 10^{-6} p$$

75°

$$0- \ 3000, \Delta R/R_0 = -2.80 \times 10^{-6} p$$
$$3000-12000, \Delta R/R_0 = -2.30 \times 10^{-6} p$$

The thermal expansions were also determined as usual, and were as follows:

Orientation	Mean linear expansion, 30°–75°	
	Extreme values	Average
90°, 1st	3.2 to 3.6 $\times 10^{-6}$	3.4 $\times 10^{-6}$
90°, 2nd	3.4 to 6.8	5.1
79°	8.0 to 8.8	8.4
56°.5	13.6 to 14.4	14.0
40°	27.5 to 29.3	28.4

Disregarding for the present the various abnormalities, certain broad features stand out. There is great difference of properties in different directions. In the cleavage plane the compressibility is less than that of iron, whereas across the plane the compressibility is more than ten times as high. This estimate is based on a rough linear extrapolation according to the $\cos^2$ law of the compressibilities of the orientations listed above, which gives for the average compressibility up to 12000 kg. the figure 19×10^{-7} for the 0° orientation. The previous conclusion about large differences of compressibility in different directions is therefore verified, but the difference turns out to be more extreme than was surmised. In the same way the linear expansion for the 0° orientation may be estimated to be about 43 $\times 10^{-6}$ against 5 or less for the 90° orientation, again showing an enormously greater deformability across the cleavage planes.

The *initial* linear compressibility for the 0° orientation may be estimated by a similar linear extrapolation to be about 27×10^{-7}. This would make the initial volume compressibility 31.6×10^{-7}. The only previous measurement of this is by Richards,[8] on polycrystalline material, who found 44×10^{-7}, so much higher than 31.6 as to be beyond

the possibility of experimental error. The difference is probably to be explained as an effect of internal strains arising from the very great differences of compressibility in different directions, and again emphasizes the conclusion that bulk measurements on haphazard aggregates of strongly non-isotropic crystals are of doubtful significance.

The average volume expansion, calculated from the linear expansions in the 90° and 0° orientations is 53×10^{-6}, or 17.7×10^{-6} for the average linear expansion of the haphazard aggregate. I. C. T. gives for this 4.7×10^{-6} from Fizeau, measured on sublimed mixed crystals. It would appear that Fizeau's orientations must have been almost exclusively the 90° orientation.

Now consider the abnormalities. These are of two sorts: seasoning effects, and breaks in the direction of the curves after complete accomodation. The seasoning effects are not universally present; one 90° and one 79° compressibility sample, and one 90° and one 83° resistance sample showed no such effects. The seasoning effects are so striking in some of the other samples, however, that it is difficult to think that the effect is entirely spurious. It may possibly be connected with the rate of cooling, and may mean that there is some other modification at high temperatures that gets carried down to room temperature into its region of instability by rapid cooling, and that the reaction then runs when the atoms are joggled, as it were, by an application of pressure. The matter requires further examination.

The other abnormality, ranges in which the behavior is linear with sharp changes in direction but no discontinuities at the points separating the ranges, is doubtless a real phenomenon, for it is shown by all the high orientations, both in compressibility and resistance. The precise details are not consistent, however, which means that this is a sensitive phenomenon. In general there seem to be three linear ranges at the 90° orientation; as the orientation changes toward zero, these phenomena rapidly disappear, and the crystal becomes normal.

Beryllium. This material I owe to the courtesy of Dr. R. Mehl, at the time Director of the Department of Metallurgy of the Naval Research Laboratory at Anacostia, D. C. The material was in the form of a lump approximately 2.5 cm. on a side; the original source was presumably the now defunct Beryllium Corporation of America. The method of formation of this lump is not known to me, but the result was a piece containing one large crystal grain, as could be established by the cleavage, which was quite perfect. This specimen was also distinguished from specimens made earlier in the art by its apparent complete homogeneity, no blow holes, slag inclusions, or

other imperfections being evident. Two specimens were worked out of the lump by grinding, one parallel and one perpendicular to the axis, each about 7.5 mm. long. Beryllium crystallizes in the hexagonal system, and has therefore a single axis of six-fold symmetry.

The compressibility results were unusual for a single crystal in that there was relatively large hysteresis between the readings obtained with increasing and decreasing pressure. The hysteresis was about the same for both specimens at both temperatures. The width of the hysteresis loop at the maximum amounted to about 2% of the total deformation. The individual points on the ascending and descending branches for the parallel specimen were regular within at most one tenth of the width of the loop; the irregularity of the other orientation was three or four times greater. The sign of the hysteresis in the changes of length was the same in both directions, so that there is also a volume hysteresis of approximately the same amount. The direction of the volume hysteresis is normal, that is, a lag, as is demanded by thermodynamics.

The numerical results follow:

Hexagonal axis parallel to the length,

$$\text{At } 30^\circ, \quad -\Delta l/l_0 = 2.20 \times 10^{-7}p - .70 \times 10^{-12}p^2,$$
$$\text{At } 75^\circ, \quad -\Delta l/l_0 = 2.30 \times 10^{-7}p - .70 \times 10^{-12}p^2.$$

Hexagonal axis perpendicular to the length,

$$\text{At } 30^\circ, \quad -\Delta l/l_0 = 2.82 \times 10^{-7}p - 1.67 \times 10^{-12}p^2,$$
$$\text{At } 75^\circ, \quad -\Delta l/l_0 = 2.82 \times 10^{-7}p - 1.70 \times 10^{-12}p^2.$$

From these results the volume compressibility may be calculated to be:

$$\text{At } 30^\circ, \quad -\Delta V/V_0 = 7.84 \times 10^{-7}p - 4.24 \times 10^{-12}p^2,$$
$$\text{At } 75^\circ, \quad -\Delta V/V_0 = 7.94 \times 10^{-7}p - 4.31 \times 10^{-12}p^2.$$

I have previously found[9] for the volume compressibility of a polycrystalline rod $8.55 \times 10^{-7}p - 3.88 \times 10^{-12}p^2$ at both temperatures. The results are not far different from those above, but indicate that the orientation of the former sample was not completely random.

The mean linear thermal expansion between 30° and 75° was found to be:

Hex. axis parallel to length, 12.3 to 14.5, average 13.4×10^{-6},
Hex. axis perpendicular, 15.2 to 17.0, average 16.1×10^{-6}.

This gives for the volume expansion 45.6×10^{-6}. The thermal expansion of Be is not listed in I. C. T.

The axial ratio of beryllium is known by X-ray analysis to be 1.585. The ratio for *spheres* in hexagonal close packing is 1.63. It would be expected therefore that the compressibility of beryllium in the two directions would not differ greatly, as turns out to be the case.

Compounds.

Gulonic Lactose. This organic substance crystallizes in the orthorhombic system, so that measurements of the linear compressibility in three different directions are necessary to exhaustively characterize the behavior under pressure. I am indebted to Mr. Phelps of the Bureau of Standards for several large clear crystals which had been grown by slow evaporation from aqueous solution. From these crystals rods varying in length from 6 to 9 mm. were cut in the three independent crystal directions "a," "b," and "c," in the nomenclature of Dana, and the compressibility measured with the lever piezometer in the usual way. Pressure was transmitted directly to the specimen with kerosene or petroleum ether, previous trials having shown no perceptible amount of solubility. Regular readings were made without incident at 30° and 75°. The average arithmetical departure from second degree curves of single readings at 30° and 75° were respectively: "a" direction, 0.22% (14 readings), and 0.29% (13 readings); "b" direction, 0.16% (13 readings), and 0.16% (15 readings); "c" direction, 0.05% (13 readings), and 0.07% (13 readings) The results are as follows:

	30°	75°
"a" direction, $-\Delta l/l_0 =$	$9.69 \times 10^{-7}p - 10.3 \times 10^{-12}p^2$;	10.66, − 11.9
"b"direction,° $-\Delta l/l_0 =$	$33.95 \times 10^{-7}p - 70.2 \times 10^{-12}p^2$;	36.67, − 81.5
"c" direction, $-\Delta l/l_0 =$	$17.02 \times 10^{-7}p - 39.9 \times 10^{-12}p^2$;	17.36, − 40.1

and by calculation, for the volume,

$$-\Delta V/V_0 = 60.66 \times 10^{-7}p - 132.0 \times 10^{-12}p^2; 64.69, -145.7$$

Rhamnose. I owe this material like the gulonic lactose, to Mr. Phelps of the Bureau of Standards, who placed at my disposal several clear crystals grown from aqueous solution. This is monoclinic and strictly specimens in four directions would be required to completely characterize the volume distortion under pressure. Unfortunately there was not enough material available to permit getting the four directions, but only the crystallographic "a," "b," and "c" directions

could be obtained. However, judging by analogy with sucrose, to be described next, and which is very similar, the missing Y direction is so much like the "a" direction that little is lost by not making a measurement on it. The specimen in the "a" direction was 4 mm. long, in the "b" direction 1.0 cm. long, and in the "c" direction 1.1 cm. The average arithmetical deviations from second degree curves of single readings at 30° and 75° were respectively: "a" direction 0.38% (16 readings), and 0.23% (15 readings); "b" direction, 0.25% (16 readings), and 0.13% (14 readings); and "c" direction, 0.15% (14 readings), and 0.16% (14 readings). The results follow:

$$\begin{array}{lll} & 30° & 75° \\ \text{"a" direction, } -\Delta l/l_0 = & 35.42 \times 10^{-7}p - 61.0 \times 10^{-12}p^2; & 37.63, -71.0 \\ \text{"b" direction, } -\Delta l/l_0 = & 21.98 \times 10^{-7}p - 38.4 \times 10^{-12}p^2; & 24.82, -53.4 \\ \text{"c" direction, } -\Delta l/l_0 = & 13.78 \times 10^{-7}p - 33.0 \times 10^{-12}p^2; & 14.66, -35.3 \end{array}$$

and by calculation, for the approximate change of volume:

$$-\Delta V/V_0 = 71.18 \times 10^{-7}p - 148.1 \times 10^{-12}p^2; \quad 77.11, -178.1$$

Sucrose (*Cane Sugar*). The source of this material was the ordinary "rock candy" of commerce. In a pound a large number of clear single crystals were found of sufficient size. This crystallizes in the monoclinic system, like rhamnose, so that four orientations are necessary. The four orientations used were the three crystallographic axes "a," "b," and "c," and the direction perpendicular to b and c, the "Y" axis of Voigt. Since the a axis is inclined at 103° to the c axis, there is a difference of only 13° between it and the Y axis, so that not much difference in compressibility in these directions is to be anticipated.

The runs on the four orientations were made without incident of any kind. The "a" sample was 5.0 mm. long, the "b" sample 9.4 mm., the "c" 7.3 mm., and the "Y" 5.6 mm. In spite of the small lengths, the compressibility is so great that large deflections were obtained, and the results are among the most regular. The average deviations from smooth curves at 30° and 75° respectively were as follows: "a" direction, 0.40 and 0.21%; "b" direction 0.43 and 0.29%; "c" direction 0.37 and 0.32%, and "Y" direction 0.47 and 0.33%. In the following the results are reproduced by second degree formulas, the constants being so chosen as to pass through the end points, and to locate at 6000 kg/cm² the maximum deviation from linearity. But this does not always represent the results within experimental error, and in a number of cases small corrections must be applied; in

general these corrections have the effect of somewhat increasing the compressibility at low pressures and decreasing it at high pressures as compared with the compressibilities of the second degree formulas. The corrections are given below in the form of deviations from the second degree formulas.

"a" direction.

30°. The maximum deviation from linearity is at 5300 instead of at 6000. At 3000, $\Delta l/l_0$ is greater numerically by 0.00005 than is given by the formula, at 6000 less by 0.00007, and at 9000 less by 0.00022.

75°. As at 30°, except that at 9000 the compressibility is less by 0.00030 instead of 0.00022.

"b" direction.

30°. The second degree formula is sufficiently good.

75°. The maximum deviation from linearity is at 5200 instead of at 6000. At 3000, $\Delta l/l_0$ is 0.00011 greater numerically than given by the formula, and at 9000 less by 0.00017.

"c" direction.

The second degree formula is sufficiently good at both temperatures.

"Y" direction.

30°. The second degree formula is sufficiently good.

75°. The maximum deviation is at 5500 instead of 6000. $\Delta l/l_0$ at 3000 is greater numerically by 0.00014 than given by the formula, and at 75° less by 0.00026.

The second degree results are:

"a" direction.

At 30°, $-\Delta l/l_0 = 32.74 \times 10^{-7}p - 69.9 \times 10^{-12}p^2$.

At 75°, $-\Delta l/l_0 = 33.80 \times 10^{-7}p - 76.3 \times 10^{-12}p^2$.

"b" direction.

At 30°, $-\Delta l/l_0 = 14.49 \times 10^{-7}p - 24.0 \times 10^{-12}p^2$.

At 75,° $-\Delta l/l_0 = 16.98 \times 10^{-7}p - 34.6 \times 10^{-12}p^2$.

"c" direction.

At 30°, $-\Delta l/l_0 = 22.81 \times 10^{-7}p - 44.4 \times 10^{-12}p^2$.

At 75°, $-\Delta l/l_0 = 24.74 \times 10^{-7}p - 52.9 \times 10^{-12}p^2$.

"Y" direction.

At 30°, $-\Delta l/l_0 = 32.00 \times 10^{-7}p - 77.5 \times 10^{-12}p^2$.
At 75°, $-\Delta l/l_0 = 33.14 \times 10^{-7}p - 78.6 \times 10^{-12}p^2$.

For the volume compressibility, from "b," "c," and "Y":

At 30°, $-\Delta V/V_0 = 69.30 \times 10^{-7}p - 161.1 \times 10^{-12}p^2$.
At 75°, $-\Delta V/V_0 = 74.86 \times 10^{-7}p - 184.2 \times 10^{-12}p^2$.

The results are seen to be numerically very close to those for rhamnose, except for a curious reversal of the b and c directions.

The thermal expansions were found to be:

Direction	Mean Linear expansion, 30°–75°.	
	Extreme values	Average
a	22.5 to 23.3 $\times 10^{-6}$	22.9 $\times 10^{-6}$
b	59.2 to 60.4	59.8
c	55.5 to 58.5	57.0
Y	21.3 to 25.3	23.3

The mean volume expansion is thus 140.1 $\times 10^{-6}$.

$MnCl_2$. This material crystallizes in the hexagonal system, but due to a misapprehension of some sort I originally supposed it to be cubic and it was measured with this idea. I probably would not have measured it if I had realized that it was hexagonal, for the values are only a sort of average, of somewhat indefinite significance. However, the measurements having been made, it seemed worth while to at least record them here.

The material in powdered condition was obtained from Eimer and Amend. It was compressed into a slug in the split mold at room temperature. (See a preceding paper for a description of the technique of forming the compressed slugs.) The material is very hygroscopic, and although precautions were taken to prevent the absorption of moisture during preparation of the specimen, treatment in the dessicator and weighing before and after heating indicated a water content of the compressibility sample of about 1%. Runs were made at 30°, 75°, and 30° again. There was a slight plastic deformation during the runs. This may have been due to two causes: in the first place there may have been some recrystallization, due to the fact that the crystal system is not cubic. In the second place, the water content

may have allowed some plastic flow under the compressive force exerted by the lever of the piezometer, an effect shown very much more prominently by the copper halides, in connection with which it has been discussed in detail in a preceding paper. This plastic flow was greatest during the first run at 30°, and during the first two low pressure readings at 75°, and amounted to about 4% of the maximum effect. It had entirely disappeared from the second run at 30°, which was the only run at 30° used in the computations. The two first points at 75° were also discarded in the computations. Because of the distortions in the specimen it did not seem worth while to try for the thermal expansion, although this had been measured for most of the other compressed slugs. The average arithmetical departure from a smooth curve of a single one of the 14 readings of compressibility at 30° was 0.14% of the maximum effect, and the corresponding figure for 13 readings at 75° was 0.18%. The results for compressibility are:

$$\text{At } 30°, \quad -\Delta V/V_0 = 54.09 \times 10^{-7}p - 96.3 \times 10^{-12}p^2,$$
$$\text{At } 75°, \quad -\Delta V/V_0 = 55.62 \times 10^{-7}p - 106.5 \times 10^{-12}p^2.$$

These volume compressibilities were calculated on the assumption of equal linear compressibility in all directions.

$ZnCl_2$. This crystallizes with the same hexagonal structure as $MnCl_2$; I also thought at first that this was cubic, and measured the linear compressibility in that misapprehension. The results are recorded here in the same spirit as those for $MnCl_2$. $ZnCl_2$ absorbs normally very large amounts of water. The water was driven off by heating as far as possible, until decomposition appeared to be just beginning, and after that it was kept in a dessicator and worked under Nujol. But according to Mellor's Chemical Handbook, it is impossible to remove all the water by heating, and the measurements bore this out.

The material was formed into a compressed slug by the technique of most of the materials of the preceding paper. Measurements were attempted only at 30°. There were enormous permanent changes of zero after each application of pressure, of which three were made altogether. Whether the permanent changes are a regrowth phenomenon connected with the water still remaining and the compressive force exerted by the lever of the piezometer, or whether they are a consequence of the non-cubic nature of the crystal, I did not attempt to decide. It seemed significant, however, that the three sets of readings with increasing pressure agreed approximately, the permanent

change taking place only on decreasing pressure. The readings on the second application of increasing pressure were made with the usual care, and showed an unusually high degree of regularity, the average arithmetical deviation from a second degree curve of a single one of the 8 readings being only 0.04% of the maximum effect. The volume change was calculated from the change of length by assuming equal compressibility in all directions, and is given for what it is worth:

$$\text{At } 30°, \quad -\Delta V/V_0 = 41.40 \times 10^{-7}p - 107.7 \times 10^{-12}p^2.$$

Al_2O_3, Synthetic Sapphire. The material was obtained from G. Everett March, a dealer in synthetic jewels of Chicago, who specially selected it from his stock. It was furnished in the form of a disc about 1.3 cm. in diameter and 3 mm. thick, the crystal axis being stated to be parallel to the plane of the disc. In appearance it was perfectly transparent and flawless. The statement about the orientation of the axis was most kindly checked for me by Professor E. S. Larsen of the Department of Mineralogy of Harvard University by optical examination, and the precise position of the axis determined. The disc was then cut without incident with a saw charged with diamond powder into rods for the compressibility measurements, a single rod 1.26 cm. long for the specimen parallel to the direction of the axis, and two pieces each 0.42 cm. long for the perpendicular orientation. These two pieces were placed end to end for the measurements.

The compressibility of the parallel sample gave an irregular curve, which could be reproduced within the error of measurement by a broken straight line, rather than the usual smooth curve. The experimental points at 30° and 75° are reproduced in Figure 8. At 30°, two complete runs were made, the first to 12000 and back with 12 readings, followed by the second with 30 readings. There was also an initial seasoning application of 12000, after which the change of zero was slightly less than after the third application of 12000, and within the limit of error of the other readings. It appears, therefore, that the effects are reproducible, approximately single valued and without hysteresis, and are not accomodation effects, but are truly characteristic of the material. At 75°, only a single application of pressure was made, but with the readings much more closely spaced than usual, 44 in all instead of the usual 14. There now appears to be a slight hysteresis between increasing and decreasing pressure, but it probably is not significant, and is of different sign at the higher and lower ends of the pressure range.

In order to reproduce the results within experimental error, it is sufficient to give the pressures at which the breaks in the curves of Figure 8 occur, and the changes of length at these pressures. Between the successive points of break the relation between pressure and change of length is linear.

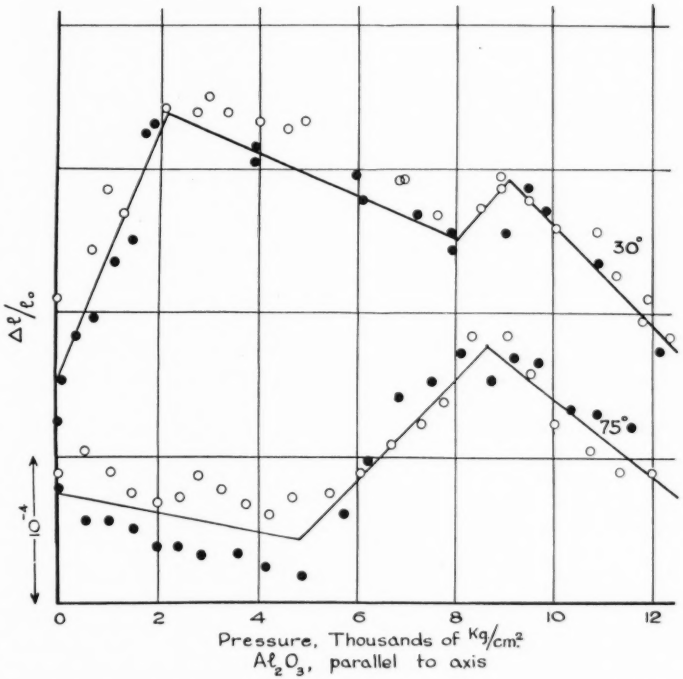

FIGURE 8. Deviations from linearity of the linear compression of Al_2O_3, crystal axis parallel to the length. The open circles are for increasing pressure and the solid circles for decreasing pressure.

At 30° the initial linear compressibility in the parallel direction is 3.9×10^{-8}, about one fifth that of iron, and at 75° it is 13.1×10^{-8}, an enormous temperature effect.

The linear thermal expansion at atmospheric pressure was determined incidentally from the zeroes of the 30° and 75° runs, as explained

TABLE II.

Al_2O_3, Parallel Orientation.

Pressure kg/cm²	$-\Delta l/l_0$
30°	
2100	0.000082
8000	.000862
9100	.000998
12000	.001362
75°	
4900	.000652
8600	.000965
12000	.001448

in the preceding paper. The mean linear thermal expansion in the parallel direction between 30° and 75° was thus found to be 9.5×10^{-6}. This is the mean of two figures, one with increasing temperature and the other with decreasing temperature, 9.7 and 9.3 respectively.

The perpendicular orientation gave nothing so striking as the parallel orientation. The experimental points are reproduced in Figure 9. There seems to be a slight amount of hysteresis at both temperatures, more, perhaps, at 75° than at 30°, as was also the case for the parallel orientation. This small amount of hysteresis was ignored in making the computations. At 30° the results lie within experimental error on a single straight line, but at 75° there would seem to be no question but that two lines, as shown, are required, with a break at 6400 kg. The results may be reproduced as follows:

Al_2O_3, perpendicular orientation.

30°

$$-\Delta l/l_0 = 1.11 \times 10^{-7} p - 0.70 \times 10^{-12} p^2$$

75°

$$\text{Below 6400,} \quad -\Delta l/l_0 = 1.39 \times 10^{-7} p - 0.70 \times 10^{-12} p^2$$

$$\text{Above 6400,} \quad -\Delta l/l_0 = .000899 + 1.01 \times 10^{-7} (p - 6400) - 0.70 \times 10^{-12} (p - 6400)^2.$$

The mean linear thermal expansion at atmospheric pressure between 30° and 75° for the perpendicular orientation was 11.6×10^{-6}, being the mean of the two values 11.7 and 11.5 with increasing and decreasing temperature. I. C. T. gives for the linear expansion at 40° 6.2 and 5.4×10^{-6} parallel and perpendicular to the axis respectively, both about half the values found for this specimen.

The initial volume compressibility at 30°, obtained by combining the results for the two orientations, is 3.17×10^{-7}. Madelung and Fuchs[10] found at 0° for synthetic sapphire 3.8. It is evident that the value 3.17 would be considerably altered if a linear extrapolation were made for the temperature effect, but in view of the many irregularities

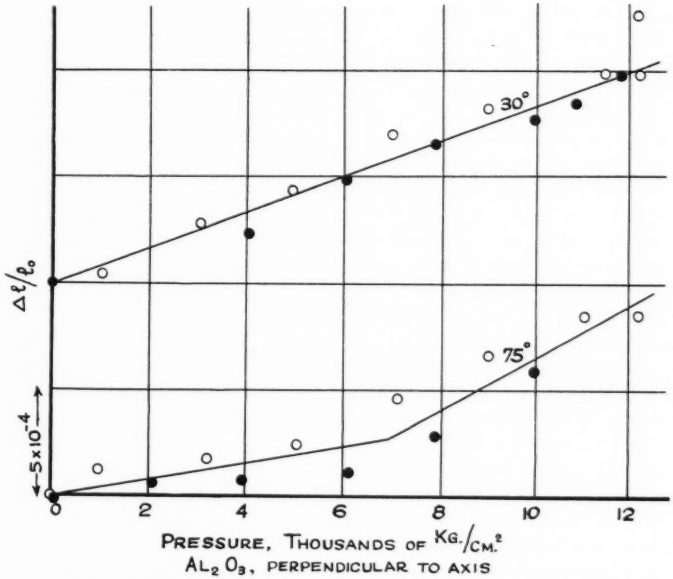

FIGURE 9. Deviations from linearity of the linear compression of Al_2O_3, crystal axis perpendicular to the length. The open circles are for increasing pressure and the solid circles for decreasing pressure.

such an extrapolation is hazardous; it is probable, however, that this specimen is distinctly less compressible than that of Madelung and Fuchs.

It was felt to be highly desirable to check these results on a specimen from another source, and to see in particular whether the breaks in the line repeat, but I was not successful in getting other suitable specimens. In this I had the assistance of Mr. B. W. St. Clair of the General Electric Co. at Lynn, who has been engaged in research on

sapphires for use in bearings of scientific instruments, and of Mr. R. H. Bird of Waltham, who specializes in the manufacture of sapphire bearings, and who has on hand a considerable stock of artificial sapphires. It appeared in the first place that artificial Al_2O_3 as it is usually supplied by the manufacturer has already experienced a spontaneous fracture due to some sort of internal strain. As it comes from the furnace, the Al_2O_3 is usually in the shape of a much elongated pear shaped drop, up to perhaps 5 cm. long and 2 cm. in diameter. This usually fractures spontaneously along some longitudinal plane. No process of annealing has yet been successful in removing the internal strains or in avoiding the fracture. The crystal axis is not simply related to the plane of fracture, but is usually inclined to it and to the length of the drop by something of the order of 45°. Mr. St. Clair was kind enough to select from his large stock two drops smaller than usual which had not experienced the usual spontaneous fracture. That each of the drops was a single crystal was beautifully evident by the appearance of the reflection pattern from the minute natural pits of the surface, a method of examination which I have often applied to metal crystals. The orientation of the crystal axes was again kindly determined by Professor Larsen, who found it to be within the expected range. He also found evidences of high internal strain, the refraction patterns being much confused, making the location of the axis difficult. These specimens were now properly mounted to give rods of the proper orientations, and Mr. Bird undertook to cut them on his diamond wheel, but both drops broke spontaneously into many pieces after the cut had penetrated only a small fraction of the total diameter. No further attempt to get other artifical specimens was made. It would appear that the specimen measured above was quite exceptional, both with regard to the location of the crystal axis with respect to the length, and with regard to freedom from internal strain, a fact which was established by Professor Larsen by his microscopic examination, and is further vouched for by the absence of any seasoning effects on the first application of pressure. Repetition of the experiment had best be made on a natural crystal, which presumably is not subject to the internal strains of the artifical crystal, but I was not able to obtain such a crystal.

Cu_6Cd_8. This is the first intermetallic compound whose compressibility I have yet measured, and it is but the beginning of an extensive projected program. This program is likely to prove arduous if many of the other compounds have as complicated behavior as this.

The compound was formed from electrolytic copper from the Bureau

of Standards and Kahlbaum's cadmium. They were reduced to fine shavings in a milling machine using a new cutter; weighed quantities were then mixed together and compressed into a slug like the com-

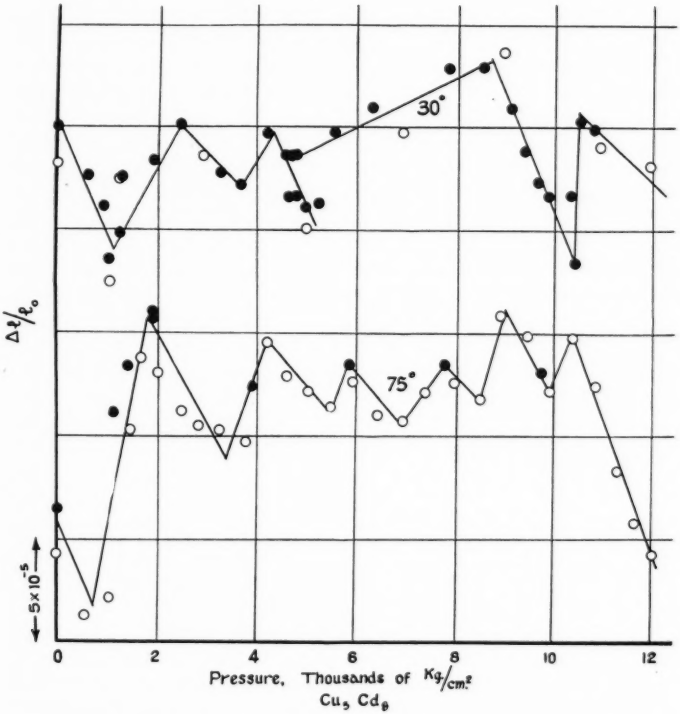

FIGURE 10. Deviations from linearity of the linear compression of Cu_3Cd_8. The open circles are for increasing pressure and the solid circles for decreasing pressure. The straight lines are to be taken merely as suggestive, and in fact a literal interpretation of the lines at 30° is not possible.

pressibility samples, which was then sealed into an evacuated quartz tube. The slug was melted at 650° C and then annealed by holding at 490° for 7 days. The outside surface did not fill the mold perfectly, but it is highly probable that there could have been no internal

cavities, for there were no appreciable seasoning effects on the first application of 12000. The annealing produced some grain growth, but the largest grains, as far as could be told from the reflection pattern of the outside surface, were not more than 2 or 3 mm. on a side. Since Cu_5Cd_8 is cubic, grain size of this magnitude should not be a factor in the final result. The specimen was formed to shape for the compressibility measurements by turning the outside surface with a diamond tool, a steel tool not being hard enough, and grinding the ends flat in the usual way.

Runs were made at 30° and 75°, and both of the runs showed an astonishing amount of fine structure. The experimental points are reproduced in Figure 10, in which the $\Delta l/l_0$ differential with respect to iron is plotted against pressure. The lines drawn in the diagram are to be taken only as roughly suggestive. It is difficult to know how much of this structure is real, and certainly difficult to know how much is significant. Detailed examination of the distribution of the points will show however that in most cases any possible hysteresis between points with increasing and decreasing pressure is much less than the scale of the structure suggested, and that there must be some sort of structure. This is by far the most complicated case of structure yet encountered. If the structure is entirely ignored, then the following average results are found for the compressibility:

$$\text{At } 30°, \quad -\Delta V/V_0 = 11.94 \times 10^{-7}p - 25.8 \times 10^{-12}p^2,$$
$$\text{At } 75°, \quad -\Delta V/V_0 = 12.29 \times 10^{-7}p - 26.1 \times 10^{-12}p^2.$$

The average linear thermal expansion at atmospheric pressure between 30° and 75° is 24.0×10^{-6}; the two runs with increasing and decreasing temperature gave 24.4 and 23.6 respectively.

The mean compressibility of the compound Cu_5Cd_8, calculated by the rule of mixtures from the compressibilities of its components, is 18.6×10^{-7} against 11.9 actual. The difference is in the direction to be expected in a compound, the forces of chemical affinity effectively increasing the internal pressure and thus decreasing the compressibility.

Alloys. A systematic attack on the problem of the compressibility of alloys would be a most elaborate undertaking, and I have not yet any such program in contemplation. However, the labor of making the compressibility measurements is comparatively so small that I have been glad to make them when the specimens of the alloys have already been prepared, usually by someone else for another purpose; the measurements here recorded were made on such specimens.

There are measurements of the Ag-Au series, and on a number of the binary alloys of Fe with W and of W with Co, selected from a rather complicated set of the ternary alloys of Fe-W-Co. The measurements brought to light a complicated situation not at all to be suggested by the known phase diagrams, so that it appears from these results that a study of compressibility may become a useful tool in the hands of the metallurgist by means of which he may discover internal changes in the composition of alloys not accessible by other methods of measurement.

Ag-Au Alloys. Three alloys of this series were measured, containing 25, 50, and 75 atomic percent of Ag. I am much indebted for them to Dr. R. Mehl, who at the time was Superintendent of the Department of Metallurgy at the Naval Research Laboratory, Anacostia, D. C., and who had them prepared under his direction. They were made up from weighed amounts, melted in vacuum, and annealed at about 920° for 40 hours. They were then forged into bars about 2.5 cm. long and 3 mm. in diameter and annealed again. The composition was not checked after preparation, so that there may have been some departure from the nominal composition, but Dr. Mehl states that any such departure could have been only slight. The bars as supplied were not quite the most convenient length for the compressibility measurements. They were accordingly lengthened by forging an additional 15%, annealed at 900° for 30 minutes, and then turned in a jeweller's lathe to true cylinders for the measurements. After the compressibility measurements had been completed, they were drawn out through steel dies, with frequent annealings in an open gas flame, to a final diameter of 0.048 cm., for the measurements of resistance. After the final size was reached they were subject to a final annealing to 900° in an electric furnace, protected by quartz tubing.

Alloy No. 1, Ag 25 A%, Au 75 A%. Measurements were made of the compressibility in the regular way at 30° and 75°. The observed displacements of the slider of the potentiometer, multiplied by a suitable constant to give approximately the differential change of length as compared with Fe, are given in Figure 11. It would seem that there can be no question that there is a break in the curve for 75° at approximately 8000 kg/cm². If it were not for the data at 75° it is doubtful whether the single markedly divergent point of the 30° series at approximately 7000 would have been interpreted as a genuine break, but in view of the 75° curve such an interpretation seems fairly secure. Table III gives the changes of volume at various

TABLE III.

RELATIVE CHANGES OF VOLUME OF ALLOY AG 25A%, AU 75A%.

Pressure kg/cm²	$\Delta V/V_0$	
	30°	75°
2000	.001281	.001254
4000	2532	2502
6000	3738	3726
8000	4959	5010
10000	6138	6207
12000	7293	7389

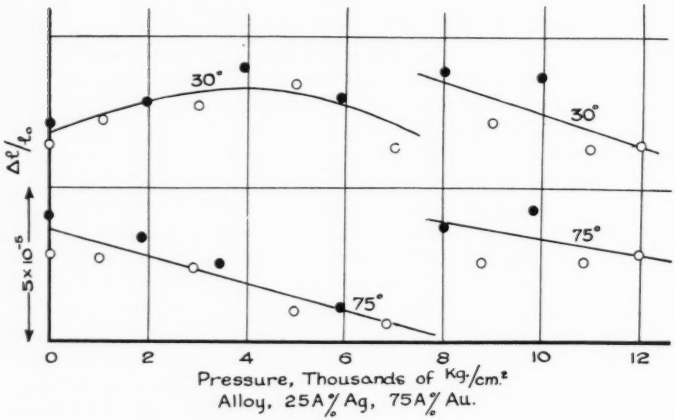

FIGURE 11. The differential linear compression of the alloy 25% Ag, 75% Au. The open circles are for increasing pressure and the solid circles for decreasing pressure.

pressures, obtained by combining the data of Figure 11 with the known compressibility of iron. At each temperature there is a break just below 8000, indicated by a horizontal line in the table; at 30° the break in $\Delta V/V_0$ is approximately 0.000039, and at 75° 0.000069. The break is in the direction corresponding to a decrease of volume with increasing pressure. This of course is necessary thermodynamically; if the sign were the opposite of that shown it would mean either that the dimensions of the rod were not changing equally in all directions, which would be curious in a fine grained material belonging to the cubic system like this alloy, or else that the apparent discontinuity

is really not abrupt, but is spread over a sufficient pressure range so that the net compressibility in the range (correcting the data of the figure for the compressibility of iron) is still negative.

The mean linear thermal expansion at atmospheric pressure between 30° and 75° was 15.3×10^{-6}; the two values obtained with increasing and decreasing temperature were 15.4 and 15.2. The agreement between these results is good, and indicates, among other things, that any permanent effects after a pressure run were very small.

The electrical resistance of wire drawn from the compressibility sample, as already explained, was measured in the regular way at 30° and 75°. Special search was made at 75° for a break in the resistance corresponding to the break in the compressibility curve. No break could be established, but the points over the entire pressure range at 75° were unusually irregular, which may have been evidence of an internal instability of some sort. The average departure from a second degree curve at 75° of a single one of the 36 readings was 0.83% of the maximum pressure effect, whereas the corresponding figure at 30° for 15 readings was 0.16%. One might at first be inclined to explain ths greater irregularity at 75° by the inadequacy of the temperature control, which is always more difficult at the higher temperature. The irregularity in the resistance just recorded for 75° would demand an *average* temperature fluctuation in the bath of 0.14°. The temperature of the bath was read with a Beckmann thermometer at the time of making each pressure reading; the *extreme* fluctuation from the mean was only .04°, and the average fluctuation somewhat less than 0.01°.

An irregularity of the change of resistance of 0.83% corresponds to 1/7000 of the total resistance. Compared with this, the break in the change of length at 75° found during the compressibility measurements was only 2 parts in 100000 on the total length. It is evident, therefore, that the compressibility measurements are very much more sensitive to small changes than are the resistance measurements. If the irregularities observed in the resistance at 75° are due to some internal change, this change must have a much smaller effect on the dimensions than on the resistance. This sort of thing is not impossible, as shown, for example, by a comparison of the numerical magnitudes of the ordinary pressure coefficient of resistance with the compressibility.

The changes of resistance given by the best smooth curves are:

$$\text{At } 30°, \; -\Delta R/R \; (0, 30°) = 1.275 \times 10^{-6}p - 0.55 \times 10^{-11}p^2,$$
$$\text{At } 75°, \; -\Delta R/R \; (0, 75°) = 1.380 \times 10^{-6}p - 0.72 \times 10^{-11}p^2.$$

The average temperature coefficient of resistance at atmospheric pressure between 0° and 100°, given by linear extrapolation of the readings at 30° and 75°, was 0.001048. The specific resistance at 30° was 8.65×10^{-6}.

Beckman[11] has measured the pressure coefficient of the Ag-Au series over a pressure range of 3000 kg., and gives curves which allow comparison with the results above by interpolation. Beckman's initial pressure coefficient at room temperature is 14.2×10^{-7} against 12.7 above. His temperature coefficient is 0.0010, and specific resistance at 30° 8.5×10^{-6}.

Alloy No. 2, Ag 50 A%, Au 50 A%. The initial application of a seasoning pressure of 12000 produced a permanent differential change of length almost 50% greater than the subsequent elastic change under 12000. After this single application of seasoning pressure, the subsequent permanent changes of dimensions were not large, as shown by Figure 12. The differences between the displacements of the slider of the potentiometer and those demanded by a linear relation with pressure, multiplied by such a constant as to give approximately the differential $\Delta l/l_0$ as compared with iron, are plotted in Figure 12. At 30° there is evidently some sort of break between 6000 and 8000. At pressures higher than this there is no perceptible hysteresis, while below it there is distinct hysteresis. At 75° the irregularities are so great that it is not quite evident what is happening; with increasing pressure there seem to be two or three distinct episodes, which are smoothed out with decreasing pressure.

The results in the following Table IV were obtained by assuming

TABLE IV.

PROPORTIONAL CHANGES OF VOLUME OF ALLOY AG 50A%, AU 50A%.

30°

Pressure kg/cm²	$-\Delta V/V_0$
2000	.001437
4000	2868
6000	4284
8000	5694
10000	6996
12000	8286

75°

$$-\Delta V/V_0 = 7.398 \times 10^{-7} p - 2.28 \times 10^{-12} p^2.$$

at 30° a break between 6000 and 8000 kg. of 0.000045 on $\Delta V/V_0$, and for the other pressures values calculated from the curve of Figure 12.

At 75° the irregularities were ignored, and the differential $\Delta l/l_0$ was taken to be linear in pressure.

The mean linear thermal expansion at atmospheric pressure between 30° and 75° was 16.6×10^{-6}. The two figures obtained with increasing and decreasing temperature were 16.7 and 16.5 respectively, close agreement.

The resistance measurements gave smooth results, with no trace of the breaks of the compressibility measurements, except possibly for

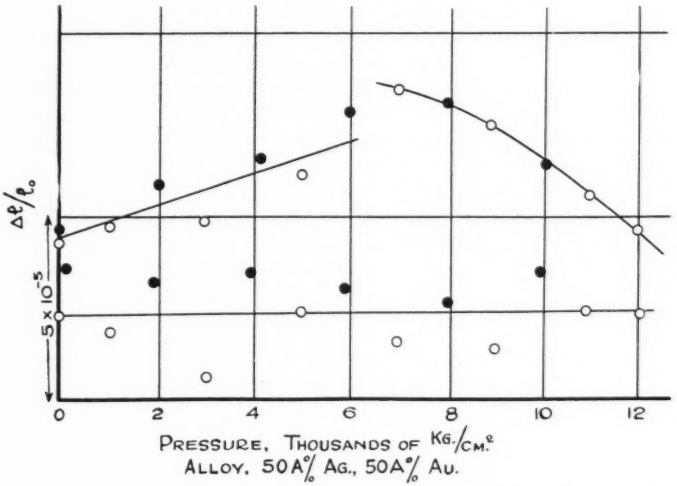

FIGURE 12. The differential linear compression of the alloy 50% Ag, 50% Au. The open circles are for increasing pressure and the solid circles for decreasing pressure. The upper points are for 30°, the lower for 75°.

the lowest two points at 75°, which fell off a smooth curve by about 1% of the total pressure effect, and were ignored in the calculations. At 30° the average arithmetical departure from a smooth curve of a single one of the 14 readings was 0.12% of the maximum effect, and at 75° the corresponding figure for 12 readings (2 discards) was 0.10%. The results were:

$$\text{At } 30^\circ, \; -\Delta R/R\,(0, 30^\circ) = 1.213 \times 10^{-6} p - 4.3 \times 10^{-12} p^2,$$
$$\text{At } 75^\circ, \; -\Delta R/R\,(0, 75^\circ) = 1.277 \times 10^{-6} p - 5.0 \times 10^{-12} p^2.$$

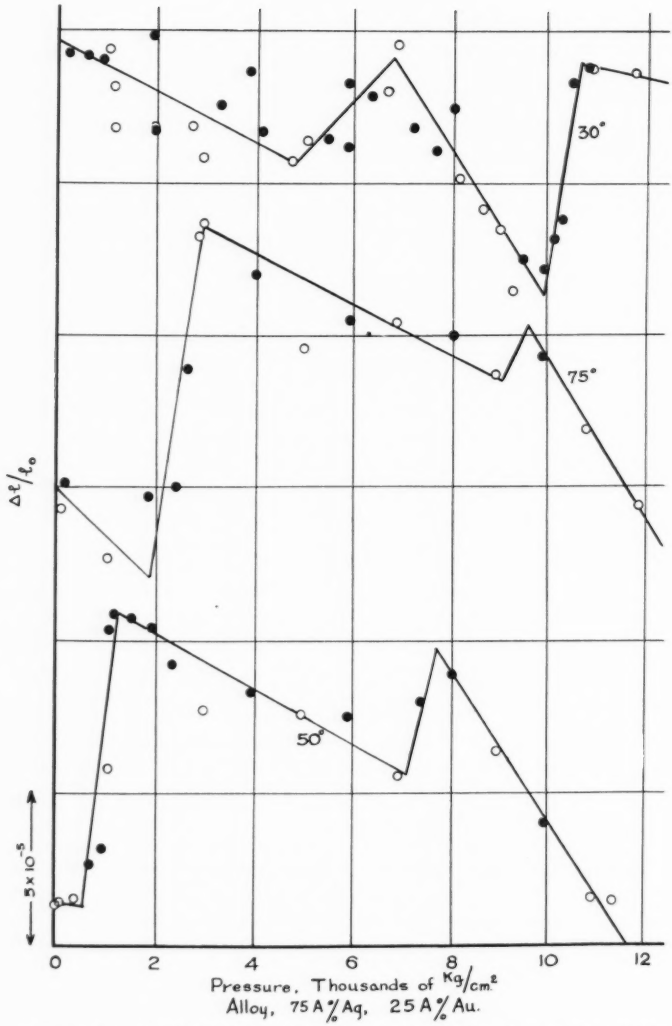

FIGURE 13. Deviations from linearity of the linear compression of the alloy 75% Ag, 25% Au. The open circles are for increasing pressure and the solid circles for decreasing pressure.

The specific resistance at 30° was 10.9×10^{-6}, and the mean temperature coefficient 0°–100°, extrapolated linearly from 30° and 75°, was 0.000774. Beckman's[11] values are: for the initial pressure coefficient 1.4×10^{-6}, for the specific resistance 10.7×10^{-6}, and for the mean temperature coefficient 0.0007.

Alloy No. 3, Ag 75 A%, Au 25 A%. The initial seasoning application of 12000 to the compressibility sample produced a permanent change of l/l_0 of 10^{-5}, which is less than 10% of the subsequent elastic differential effect. This is somewhat surprising in view of the complicated state of affairs revealed by the later measurements. Readings were first made in the regular way at 30° and 75°, and then, because of the complications, a run was inserted at 50°. The difference between the actual displacement of the slider of the potentiometer and the displacements that would have been found if the relation with pressure had been linear, multiplied by such a constant as to give approximately the differential change of length with reference to iron, are given in Figure 13. The results can be reproduced nearly within the limits of error by the broken straight line drawn. In Table V the volumes are given at the various break points of these lines; between the break points the volumes are to be found by linear interpolation.

TABLE V.

PROPORTIONAL CHANGES OF VOLUME OF ALLOY AG 75A%, AU 25A%.

Pressure kg/cm²	$-\Delta V/V_0$
30°	
4900	00388
6900	558
10000	788
10700	860
12000	958
50°	
560	00047
1200	00127
7100	596
7700	657
12000	970
75°	
1900	00152
3000	248
9100	771
9600	813
12000	989

The mean linear thermal expansion at atmospheric pressure between 30° and 75° was 20.2×10^{-6}; the two values obtained with increasing and decreasing temperature were 20.3 and 20.1.

The resistance measurements showed no trace of the anomalies of the compressibility measurements. At 30° the average arithmetical deviation from a second degree curve of a single one of the 16 readings was 0.15% of the maximum effect, and at 75° the corresponding figure for 14 readings was 0.20%. The results are:

$$\text{At } 30°, \; -\Delta R/R\,(0, 30°) = 1.301 \times 10^{-6}p - 5.1 \times 10^{-12}p^2,$$
$$\text{At } 75°, \; -\Delta R/R\,(0, 75°) = 1.410 \times 10^{-6}p - 6.9 \times 10^{-12}p^2.$$

The mean temperature coefficient of resistance at atmospheric pressure between 0° and 100°, by linear extrapolation of readings at 30° and 75°, was 0.000888, and the specific resistance at 30°, 8.64×10^{-6}.

Beckman[8] found for the initial pressure coefficient of resistance 1.5×10^{-6}, for the temperature coefficient 0.0008, and for the specific resistance at 30° 8.7×10^{-6}.

Co-Fe-W alloys. Mr. Bruce A. Rogers had made up some 30 of the ternary alloys with the special object of studying the magnetic behavior. The alloys were melted in the laboratories of the Western Electric Co., in Chicago, in a vacuum furnace. The magnetic measurements were made in the Cruft Laboratory of Harvard University and will be reported elsewhere. Mr. Rogers was kind enough to place this material at my disposal, and from it I selected three binary alloys of Fe and W and three binary alloys of W and Co as most interesting. It seemed to me not worth the labor to measure all the ternary alloys, in view of the fact that a study of the compressibility of even binary alloys has hardly yet begun. I did, however, measure that one of the ternary alloys which the magnetic work of Mr. Rogers had suggested to be the most likely to show interesting effects. It did not disclose any peculiarities in the compressibility corresponding to the peculiarities in the magnetic behavior, and the subject was not pushed further.

The percentage compositions given in the following are nominal and approximate weight percentages; they were determined from the amounts of the constituents before alloying. The actual compositions of the final alloys were determined by special analysis made by Mr. Walter M. Saunders of pieces milled from the forgings and were as follows:

Nominal Composition weight per cent.			Actual Composition weight per cent.		
W	Co	Fe	W	Co	Fe
10	0	90	10.05	—	—
20	0	80	20.03	—	—
30	0	70	27.93	—	—
10	90	0	9.83	87.38	2.30
20	80	0	15.15	82.82	2.30
30	70	0	30.01	67.40	2.46
30	10	60	30.16	10.75	—

In addition the common impurities were determined in an alloy selected at random, which should be roughly typical of the lot, and were found to be: Carbon, 0.02%, Manganese 0.007, Phosphorus 0.004, Sulphur 0.009, Silicon 0.03, Nickel trace, Copper trace.

After melting, which was done in a Northrup induction furnace, the contents of the crucible were forged to flat discs about 1 cm. thick and 10 cm. in diameter. In the following, "unannealed" refers to the condition as left by forging. The annealing was done by Mr. Rogers by heating either in a vacuum or in an atmosphere of hydrogen at approximately atmospheric pressure to 1050° for 5 hours and slowly cooling in the furnace.

Fe 90%, W 10%. This alloy was measured both before and after annealing. Before annealing the Rockwell hardness numbers, B scale, measured at four places varied from 57.5 to 65.8. After annealing they were from 49.6 to 56.1.

Unannealed specimen. This was subjected to a preliminary seasoning application of 11500, and a second one of 9000. The total permanent change of zero after the second application was about twice the total elastic effect at 30° shown in the figure. This seasoning appeared to be effective and there were no further permanent changes. The potentiometer displacements, multiplied by the proper constant to give roughly the differential $\Delta l/l_0$ with respect to Fe, are shown in Figure 14. It is to be noticed in this and all similar diagrams of this paper that the exact calculations cannot be made from the diagrams alone, because certain important corrections are not indicated, which often are of the same order of magnitude as the displacements of the figures. At 30° the points lie smoothly and the differential compression with respect to Fe is linear in the pressure. At 75°, on the other hand, there are two distinct episodes in the behavior. Above 8000 the relation between pressure and differential compression

is linear, without hysteresis, and with the same slope as at 30°, meaning a smaller compressibility than that of iron. Below 8000, on the other hand, there is hysteresis, and the average compressibility is greater than that of iron. It is especially to be noticed that this hysteresis in the length is in the abnormal direction, following, instead of lagging behind the pressure. It is thermodynamically impossible that the volume change should lag in this way, which means that the changes of length giving rise to this hysteresis cannot be uniform in all directions. The maximum width of the hysteresis loop corresponds to a $\Delta l/l_0$ of 0.000110.

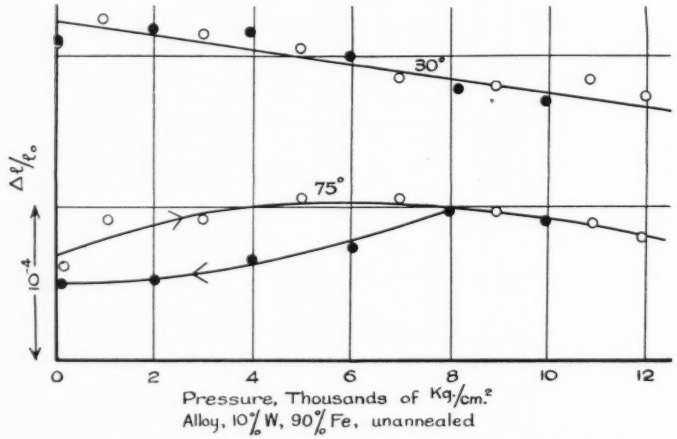

FIGURE 14. The differential linear compression of the alloy, 10% W, 90% Fe, unannealed. The open circles are for increasing pressure and the solid circles for decreasing pressure.

In the following the formula ignores the hysteresis, assuming the linear relation shown by the straight line drawn through the center of the loop. The results follow:

At 30°, $-\Delta V/V_0 = 5.712 \times 10^{-7}p - 2.22 \times 10^{-12}p^2$.

At 75°. Between 0 and 8000 kg/cm², ignoring hysteresis,

$$-\Delta V/V_0 = 5.617 \times 10^{-7}p - 2.22 \times 10^{-12}p^2.$$

Between 8000 and 12000,

$$-\Delta V/V_0 = .004353 + 5.462 \times 10^{-7}\,(p - 8000) - 2.22 \times 10^{-12}\,(p - 8000)^2.$$

Annealed Specimen. After the measurements recorded above the specimen was annealed at 1050° in vacuum for 5 hours.

The curves of approximate differential compressibility corresponding to Figure 14 are shown in Figure 15. Notice that the scale is different. The general character is not much altered. A slight amount of hysteresis appears at 30°. This agrees with the general experience of Mr. Rogers, who finds that the results of annealing are often anomalous, the material after annealing being apparently further

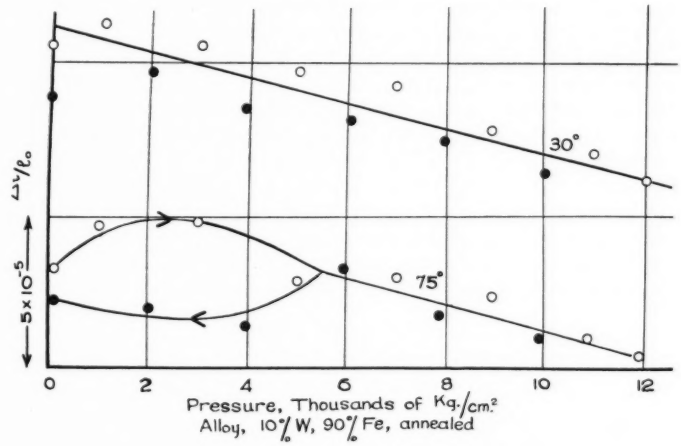

FIGURE 15. The differential linear compression of the alloy 10% W, 90% Fe, annealed. The open circles are for increasing pressure and the solid circles for decreasing pressure.

from a state of internal equilibrium than before. This probably indicates the action of some very slow internal change at the annealing temperature, such that a very much longer annealing than that actually given would have been necessary to attain complete equilibrium, and even then there is every reason to think that there are further changes at lower temperatures, so that behavior at room temperature need not be entirely free from hysteresis, even after infinitely long seasoning at a single temperature. The 75° curve of Figure 15 is generally similar to that of Figure 14. There is hysteresis at the lower pressures; the pressure at which the hysteresis loop

closes has been displaced from 8000 to about 6000. The maximum width of the hysteresis loop corresponds to a $\Delta l/l_0$ of 0.000049. Again the hysteresis is in the abnormal direction. The results follow:

At 30°, $-\Delta V/V_0 = 5.433 \times 10^{-7}p - 2.19 \times 10^{-12}p^2$.

At 75°, entirely ignoring the hysteresis loop and using the slope given by the straight line in Figure 15,

$$-\Delta V/V_0 = 5.535 \times 10^{-7}p - 2.19 \times 10^{-12}p^2.$$

In addition to the effects already discussed it is to be noticed that annealing has decreased the compressibility somewhat.

Fe 80%, W 20%, unannealed. The Rockwell hardness, C scale, varied from 3.8 to 8.2. This was seasoned by a preliminary application of 12000, but the accompanying change of dimensions was not recorded. The displacements of the potentiometer slider of the regular runs, multiplied by such a constant as to give roughly the differential $\Delta l/l_0$ with respect to iron, are plotted in Figure 16. There is practically no hysteresis, but a very distinct pattern and departure from linearity. The experiment was now tried of shortening the specimen and repeating the measurements at 30°. It was shortened by 0.002 inches, which is 13 times the differential change of length under 12000.

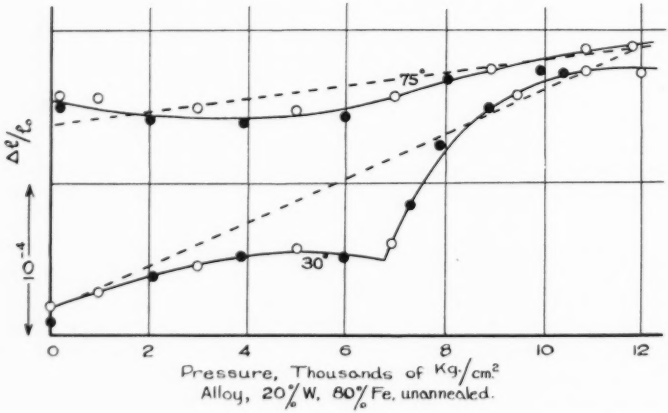

FIGURE 16. The differential linear compression of the alloy 20% W, 80% Fe, unannealed, first run. The open circles are for increasing pressure and the solid circles for decreasing pressure.

This changed the position of the lever of the piezometer so that an entirely different part of the slide wire was engaged, and provided a test as to whether the pattern was due to irregularities in the slide wire or to irregularities in the pivot of the lever at that particular part of its motion. The first run with the shortened specimen gave irregular results with a break at approximately the same pressure as the second. The second run gave the curve of Figure 17, which has essentially the same character as the 30° of Figure 16 although the pressure of the break is somewhat displaced.

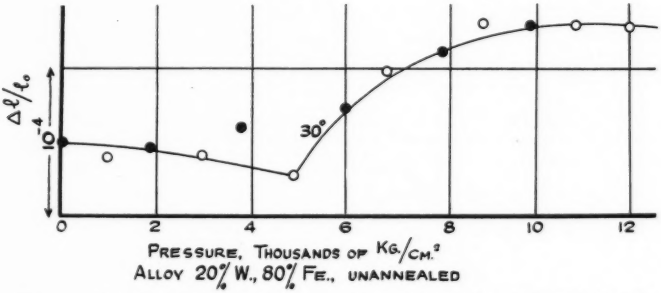

FIGURE 17. The differential compression of the alloy 20% W, 80% Fe, unannealed, shortened, second run. The open circles are for increasing pressure and the solid circles for decreasing pressure.

Smoothed results were computed by entirely ignoring the breaks and using for 30° and 75° the two straight lines indicated in Figure 12. These give:

$$\text{At } 30°, \; -\Delta V/V_0 = 5.139 \times 10^{-7}p - 2.19 \times 10^{-12}p^2,$$
$$\text{At } 75°, \; -\Delta V/V_0 = 5.559 \times 10^{-7}p - 2.19 \times 10^{-12}p^2.$$

Superposed on the ΔV given by the formulas are small scale effects determined by the curves. At 30° the maximum departure is at 7000 and is 0.000780 for $\Delta V/V_0$, the actual ΔV at 7000 being less arithmetically than given by the formula. At 75° the maximum deviation is at about 6000, the $\Delta V/V_0$ here being less arithmetically by 0.00039 than given by the formula.

Annealed specimen. The specimen was now annealed for five hours in vacuum at 1050°, and the behavior was very materially changed. Its Rockwell hardness, C scale, varied from 2.0 to 8.5. The displacements, multiplied by the proper constant to give approximately

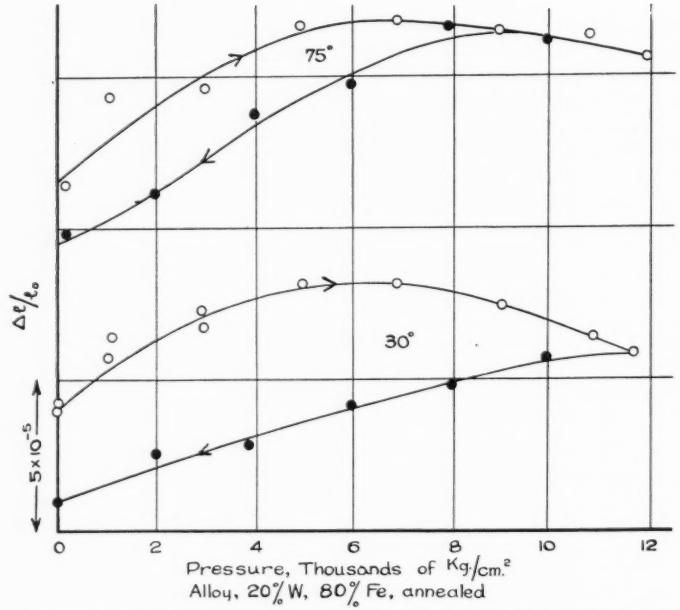

FIGURE 18. The differential linear compression of the alloy 20% W, 80% Fe, annealed. The open circles are for increasing pressure and the solid circles for decreasing pressure.

TABLE VI.

PROPORTIONAL CHANGES OF LENGTH OF ALLOY Fe 80%, W 20%, ANNEALED.

Pressure kg/cm²	$-\Delta l/l_0$	
	30°	75°
2000	.000348	.000354
4000	701	708
6000	.001057	.001066
8000	1414	1431
10000	1772	1790
12000	2126	2146
10000	1784	1790
8000	1442	1434
6000	1097	1085
4000	747	732
2000	390	381
0	−29	−17

$\Delta l/l_0$ are reproduced in Figure 18. There is now large hysteresis. Further, this hysteresis is in the abnormal direction, indicating that this is not a true bulk effect, but there must be preferential directions. The only satisfactory way to reproduce these results is by a table, giving the changes of length with increasing and decreasing pressure.

The average compressibility has been considerably increased by the annealing; the total change of length at 30° for 12000 kg. before annealing was 0.00195 against 0.00213 after annealing. It is not surprising that a change of internal structure great enough to change the total compressibility by this amount should wipe out the pattern shown in Figure 16, and replace it by a different pattern as in Figure 18.

Fe 70%, W 30%. Two batches of alloy of this approximate composition were made; in one the W content was less than 30% by an inconsiderable amount, and in the other it was slightly greater than 30%. These will be referred to as the "W low" and the "W high" specimens respectively.

Unannealed Specimens. The Rockwell hardness, C scale, varied from 7.2 to 11.2, and from 21.5 to 24.7 for the "low" and the "high" specimens, respectively. They were both measured first in the unannealed condition, and the results are shown in Figure 19, in which the approximate differential $\Delta l/l_0$ is given against pressure, as usual. It will be seen that both specimens give essentially the same results; a curve smooth within limits of error and with only small hysteresis at 30°, but a 75° curves with a distinct break in the neighborhood of 2000 kg. It will be noticed that the "high" specimen shows evidence of a displacement of the break to very low pressures at 30°. It may well be that as a consequence of slight difference of chemical composition the break is displaced a little further with the "low" specimen, below atmospheric pressure, and so does not show on the diagram. The essential agreement of the results with these two specimens affords further welcome proof of the reality of these small effects. If one disregards to a first approximation the discontinuity at 75°, computing from the smooth curve, and taking the average for the two specimens, the following will be found:

$$\text{At } 30°, \quad -\Delta V/V_0 = 4.752 \times 10^{-7}p + 1.53 \times 10^{-12}p^2,$$
$$\text{At } 75°, \quad -\Delta V/V_0 = 4.401 \times 10^{-7}p + 3.66 \times 10^{-12}p^2.$$

Notice the abnormal sign of the second degree term, the significance being a compressibility increasing with increasing pressure. At 75° the results given by the formula should be corrected by the small amounts suggested by the curve of Figure 19 to get ΔV to a

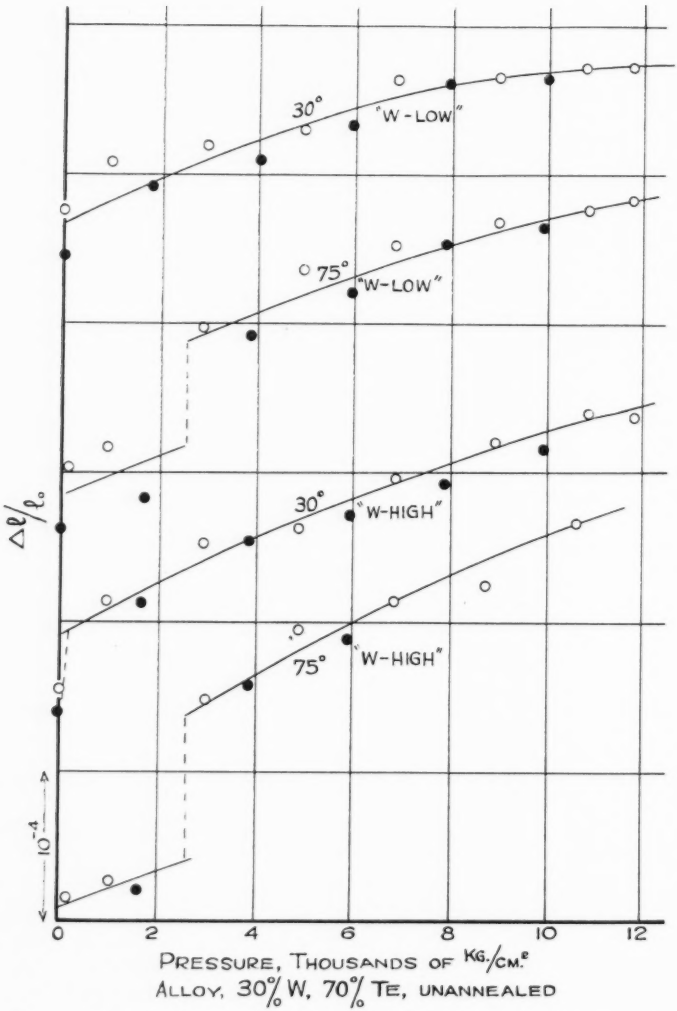

FIGURE 19. The differential linear compression of the alloy 30% W, 70% Fe, unannealed. The open circles are for increasing pressure and the solid circles for decreasing pressure.

precision high enough to show the small scale effects. But the accurate numerical values of the small scale effect can not be taken from the figure, as already explained, because the figure neglects certain important corrections. The accurate value of the discontinuity in $\Delta l/l_0$ at 75° is 0.000155 in the direction of a decrease of length, which involves a decrease of volume as demanded by thermodynamics. If account is taken of the discontinuity, the initial compressibility at 75° becomes 4.47 instead of 4.40×10^{-7}.

Annealed specimens. The specimens were now annealed at 1050° in vacuum for five hours. The Rockwell hardness, C scale, was now 7.5 to 9.1 and 26.8 to 27.0, respectively. The behavior is entirely altered, as shown in Figure 20, and although the behavior of the two specimens still show resemblances, they are more different than they were before annealing. This suggests again that the annealing time is not long enough, and that important internal changes take place during the cooling, which was not slow enough. The best way to reproduce the results is by a table, giving the two specimens separately.

TABLE VII.

RELATIVE CHANGES OF LENGTH OF TWO SPECIMENS OF ALLOY FE 70%, W 30%, AFTER ANNEALING.

Pressure kg/cm²	"W low" specimen $-\Delta l/l_0$		"W high" specimen $-\Delta l/l_0$	
	30°	75°	30°	75°
2000	.000344	.000349	.000300	.000328
4000	674	695	619	657
6000	.001018	.001036	956	976
8000	1354	1369	.001289	.001316
10000	1696	1698	1616	1650
12000	2030	2048	1936	1975
10000	1710	1726	1636	1656
8000	1379	1396	1313	1328
6000	1045	1062	984	996
4000	713	725	640	688
2000	383	373	323	350
0	−42	−14	−43	−10

The effect of annealing this alloy has been to decrease somewhat the mean compressibility up to 12000.

W, Co Alloys. These alloys were all measured only in the annealed condition. The three different alloys were annealed in hydrogen at 985° for five hours and cooled slowly in the furnace.

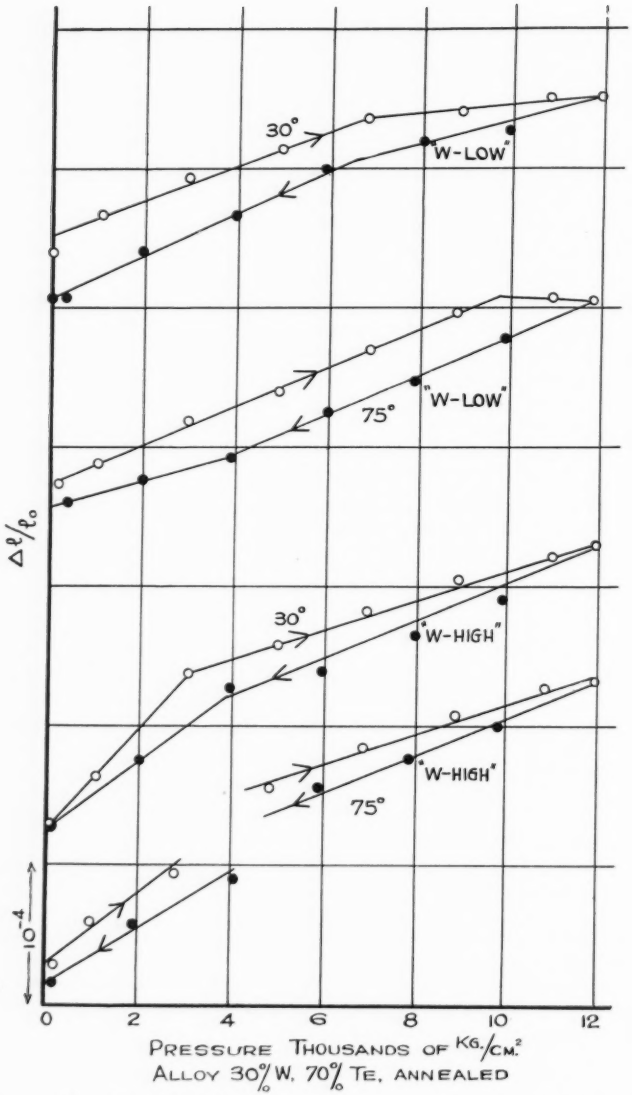

FIGURE 20. The differential linear compression of the alloy 30% W, 70% Fe, annealed. The open circles are for increasing pressure and the solid circles for decreasing pressure.

W 10%, Co 90%. The Rockwell hardness, C scale, was between 6.8 and 11.0. The first seasoning application of 12000 to this changed the zero by an amount just detectible on the slide wire and less than the normal irregularity of a single reading. Runs were made at 30°

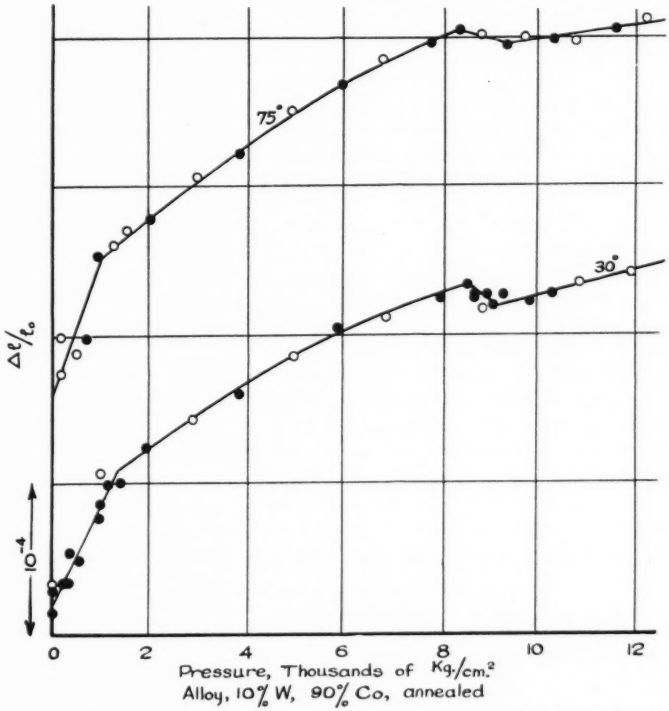

FIGURE 21. The differential linear compression of the alloy 10% W, 90% Co, annealed. The open circles are for increasing pressure and the solid circles for decreasing pressure.

and 75°. The approximate differential changes of length with respect to iron are shown in Figure 21. There is practically no hysteresis, in marked contrast to the Fe-W series. Obviously the results cannot be reproduced by a simple formula, and the changes of volume are therefore given as a function of pressure in Table VIII.

TABLE VIII.

PROPORTIONAL CHANGES OF VOLUME OF ALLOY W 10%, Co 90%.

Pressure kg/cm²	$-\Delta V/V_0$ 30°	75°
1000	.000351	.000300
2000	792	786
3000	.001269	.001263
4000	1761	1755
5000	2235	2232
6000	2724	2721
7000	3210	3207
8000	3702	3702
9000	4236	4230
10000	4740	4764
11000	5214	5268
12000	5694	5763

W 20%, Co 80%. The Rockwell hardness, C scale, was between 22.8 and 28.5. On the first application of 12000 seasoning pressure there was a permanent change of l/l_0 of 0.000017. The readings of the regular runs at 30° and 75°, multiplied by such a constant as to give approximately the differential $\Delta l/l_0$ with respect to iron, are shown in Figure 22. There is no hysteresis within the limits of error. There is some sort of a break at a mean pressure of 5100 at 30° and 5600 at 75°. The magnitude of the break means a $\Delta l/l_0$ of 0.000021, and the direction corresponds to an *increase* of length. If this increase of length were equal in all directions, and were truly abrupt, it would mean an increase of volume, which is impossible thermo-

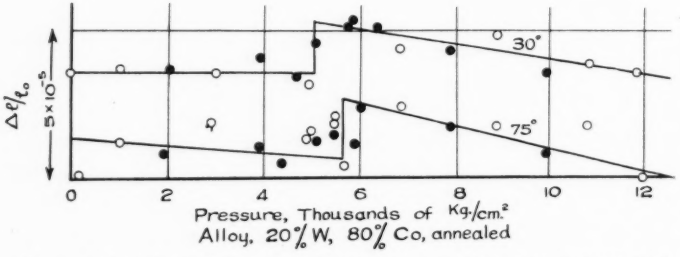

FIGURE 22. The differential linear compression of the alloy 20% W, 80% Fe, annealed. The open circles are for increasing pressure and the solid circles for decreasing pressure.

dynamically. There are two possible solutions; either the increase of length does not take place uniformly in all directions, there being compensating decreases in other directions, or else the change is not truly abrupt, but is spread over a range of pressure wide enough to give a total decrease of volume on combining the compressibility of Fe with the differential compressibility of the alloy. The numerical values demand that the transition region be at least 100 kg. wide, and this does not seem to be at all impossible.

Above and below the region of the break the relation between pressure and differential $\Delta l/l_0$ is approximately linear, although at the lower pressures at 75° there may be some departures. Assuming the linear relation, the following are the numerical results of the measurements:

At 30°, Below 5100, $-\Delta l/l_0 = 1.691 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$.

At 5100, or in a range centering on 5100, there is an increase of l/l_0 of 0.000017.

Above 5100, $-\Delta l/l_0 = .000030 + 1.717 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$.

At 75°, Below 5600, $-\Delta l/l_0 = 1.719 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$.

At 5600, or in a range centering on 5600, there is an increase of l/l_0 of 0.000021.

Above 5600, $-\Delta l/l_0 = .000033 + 1.744 \times 10^{-7}p - 0.70 \times 10^{-12}p^2$.

W 30%, Co 70%. The Rockwell hardness, C scale, was between 44.5 and 46.0. The permanent change of relative length on the first seasoning application of 12000 was − 0.000027. Runs were made at 30°, 75°, and at 30° again up to 5000, repeating the first part of the first run, which was essentially checked. The slider displacements at 30° and 75°, multiplied by such a constant as to give approximately the differential $\Delta l/l_0$ are shown in Figure 23. The pattern is more complicated than for the two previous alloys, but again there is no hysteresis within limits of error. The results are reproduced in Table IX. In this table are given the pressures at which occur the various cusps of the broken lines of Figure 23. Between the pressures of the cusps the relation between $\Delta l/l_0$ and pressure can be assumed to be linear with sufficient accuracy, although a very slight amount of curvature is indicated in the figure in the two segments at the highest pressures at 75°.

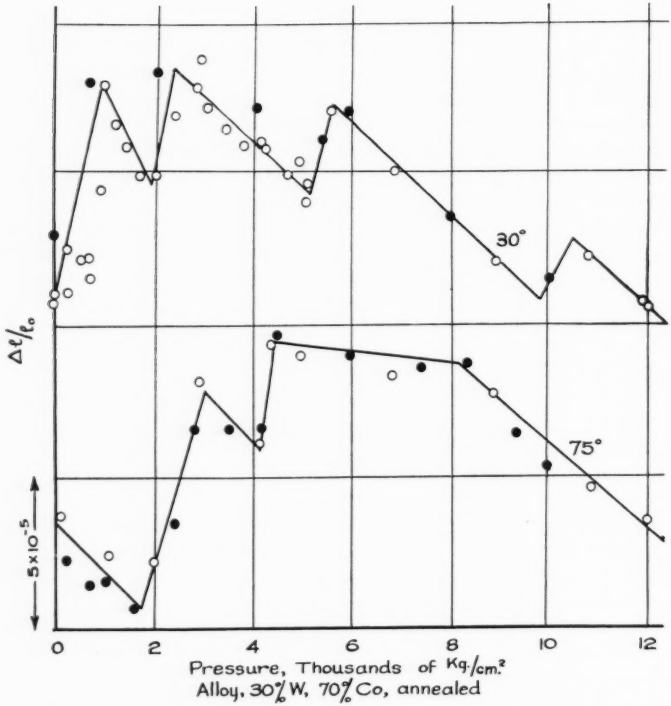

FIGURE 23. The differential linear compression of the alloy 30% W, 70% Co, annealed. The open circles are for increasing pressure and the solid circles for decreasing pressure.

TABLE IX.

RELATIVE CHANGES OF LENGTH OF ALLOY W 30%, Co 70%.

Pressure kg/cm²	$-\Delta l/l_0$	Pressure kg/cm²	$-\Delta l/l_0$
30°		75°	
880	.000065	1660	.000325
1900	.000235	2990	427
2350	278	4110	613
5180	735	4420	630
5630	771	8400	.001228
9880	.001438	12000	1797
10520	1504		
12000	1723		

Fe 60%, W 30%, Co 10%. As already stated, this is that one of the ternary alloys which Mr. Rogers had found to show the most complicated magnetic behavior. Three sets of measurements were made on this alloy: in the unannealed condition after forging, after annealing at 670° C for 5¼ hours and cooling in the furnace, and after annealing for 5 hours in vacuum at 1050° and cooling in the furnace. The first measurements on the unannealed specimen showed nothing of interest, the relation between pressure and potentiometer setting being linear within experimental error. At 30° the average arithmetical deviation from a straight line of a single one of the 13 readings is 0.53% of the maximum effect, and at 75° the corresponding figure is 0.31% for 14 readings. The only exception is the single reading at 30° and 12000 kg/cm², which departs from a line by six times the average deviation of the other points, and may indicate a real effect. Neglecting this point, the results are:

Before annealing.

$$\text{At } 30°, \quad -\Delta V/V_0 = 5.31 \times 10^{-7}p - 2.2 \times 10^{-12}p^2,$$
$$\text{At } 75°, \quad -\Delta V/V_0 = 5.62 \times 10^{-7}p - 2.2 \times 10^{-12}p^2.$$

After the first annealing at 670° the results were little changed. Most of the readings again lay on a straight line; at 30° the average arithmetical deviation from a straight line of a single one of the 12 readings was 0.33% of the total effect, and at 75° the corresponding figure for 15 readings was 0.36%. Again the only exception was at 30°, where now the three highest points, at 10000, 11000, and 12000 lay above the curve by 10 times the average deviation of the other points, corresponding to a discontinuity in $\Delta l/l_0$ of 0.000075. The effect is doubtless real, and means some sort of internal change at the high pressure end of the 30° isotherm, the effect of annealing at 670° being to depress somewhat the pressure at which this change occurs. Neglecting this transition, and assuming a linear relation, the results are:

After annealing at 670°,

$$\text{At } 30°, \quad -\Delta V/V_0 = 5.24 \times 10^{-7}p - 2.2 \times 10^{-12}p^2,$$
$$\text{At } 75°, \quad -\Delta V/V_0 = 5.28 \times 10^{-7}p - 2.2 \times 10^{-12}p^2.$$

The effect of annealing at 670° has been to decrease the mean compressibility slightly.

The second annealing at 1050° materially altered the behavior, and introduced hysteresis effects and permanent changes, just as the

annealing of the Fe-W alloys did. In all, five applications of pressure were made at 30° and 75°, the results of which are shown in Figure 24. There is no point in trying to reproduce the details of the hysteresis. If the mean curves indicated by the dotted lines are used in the computation, the results given in Table X will be found.

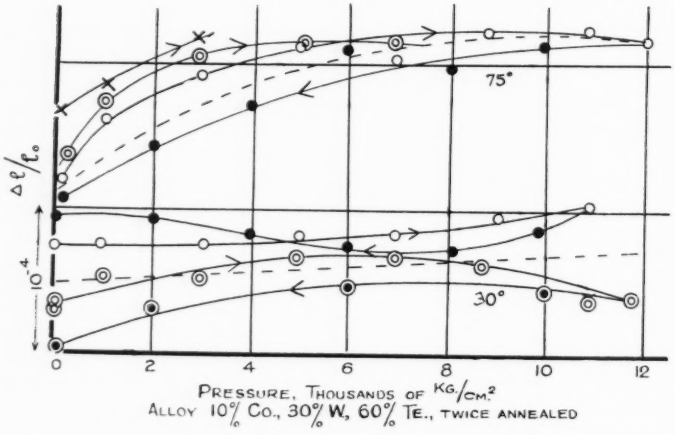

FIGURE 24. The differential linear compression of the alloy 10% Co, 30% W, 60% Fe, twice annealed. The significance of the points is as follows. At 30°: open circle, first increase; solid circle, first decrease; double open circle, second increase; double circle, solid core, second decrease. At 75°: Cross, first increase; double circle, second increase; single open circle, third increase; single solid circle, third decrease.

TABLE X.

RELATIVE CHANGES OF LENGTH OF ALLOY FE 60%, W 30%, CO 10% AFTER ANNEALING AT 1050°.

Pressure	$-\Delta l/l_0$	
kg/cm²	30°	75°
2000	.000365	.000338
4000	714	681
6000	.001077	.001027
8000	1425	1375
10000	1767	1726
12000	2104	2075

At 30° the results can also be indicated by the formula:

$$-\Delta V/V_0 = 5.51 \times 10^{-7}p - 2.3 \times 10^{-12}p^2.$$

The annealing has now increased the compressibility by a slight amount.

Discussion.

This discussion will be almost entirely concerned with the anomalous behavior of the various substances; the normal substances at the beginning of the paper have already been sufficiently commented on in the detailed exposition of the data. All that can be attempted with regard to the discontinuities is a discussion of the thermodynamics involved and a few very general remarks.

The basic thermodynamics has already been discussed in connection with the anomalies of NH_4Cl.[12] It was there shown that if there is a break in direction (discontinuity in the first derivative) of the curves of volume against pressure at constant temperature, then there is a relation between the increments of pressure and temperature at which the break occurs which is the exact analogue of Clapeyron's equation, and is $d\tau/dp = \tau dv/dQ$. dv/dQ is the ratio of volume change to heat absorbed by whatever the process is which is responsible for the break. There is now one important remark to be made about the thermodynamics of the situation which was not made in the previous analysis. It is well known that the discontinuities in the volume itself, such as occur when a system changes from one phase to another, are subject to the thermodynamic restriction that the phase stable at the higher pressure must have the smaller volume, or in other words, any discontinuity in volume brought about by increasing pressure must be a volume decrease. It might at first impulse be thought that there should be a similar restriction on any discontinuities in the direction of the isotherm (that is, in the derivative of the volume with respect to pressure at constant temperature), so that only discontinuities of the kind indicated in Figure 25 should be possible, that is, only discontinuities in which the internal change brought about by increasing pressure runs with decreasing volume. This however, is not the case. The relation above is a geometrical one, the only intervention of thermodynamics in the derivation of the formula occurring when $\left(\frac{\partial v}{\partial \tau}\right)_p$ is replaced by $-\frac{1}{\tau}\left(\frac{\partial Q}{\partial p}\right)_\tau$. This thermodynamic relation contains no restriction as to sign, and the generalized Clapeyron equation may be regarded as a geometrical one

determining dQ in terms of any possible values of $d\tau$, dp, and dv. A detailed examination will show that the only restriction as to sign which thermodynamics imposes is merely in demanding that the slope of the isotherms be negative, that is, that the compressibility be negative. In Figure 26 are shown the various geometrical possibilities with regard to the relative location of the various isotherms;

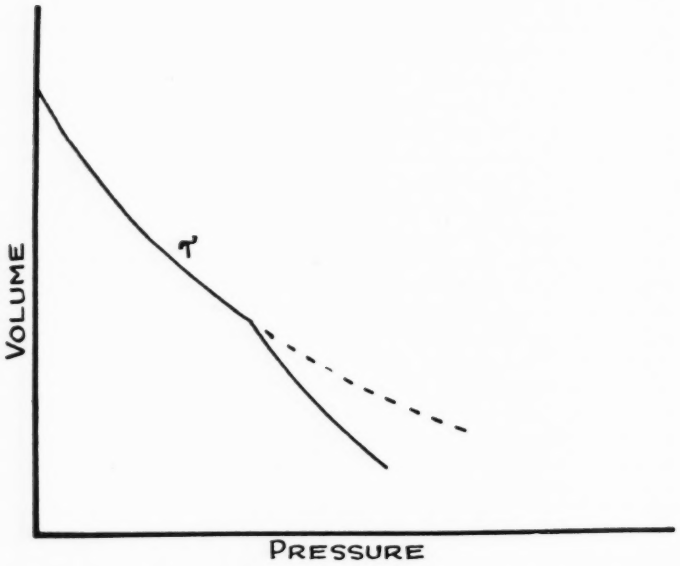

FIGURE 25. One possible kind of discontinuity in the volume-pressure isotherm.

to each of these geometrical possibilities corresponds a case with $d\tau$ either positive or negative, so that physically there are 16 qualitatively different cases.

From the point of view of a single isotherm, all this merely means that the compressibility may either increase or decrease on passing with increasing pressure through a point of discontinuity in the derivative. This is only natural, because of course it is well known that there is no thermodynamic reason why the compressibility of a substance

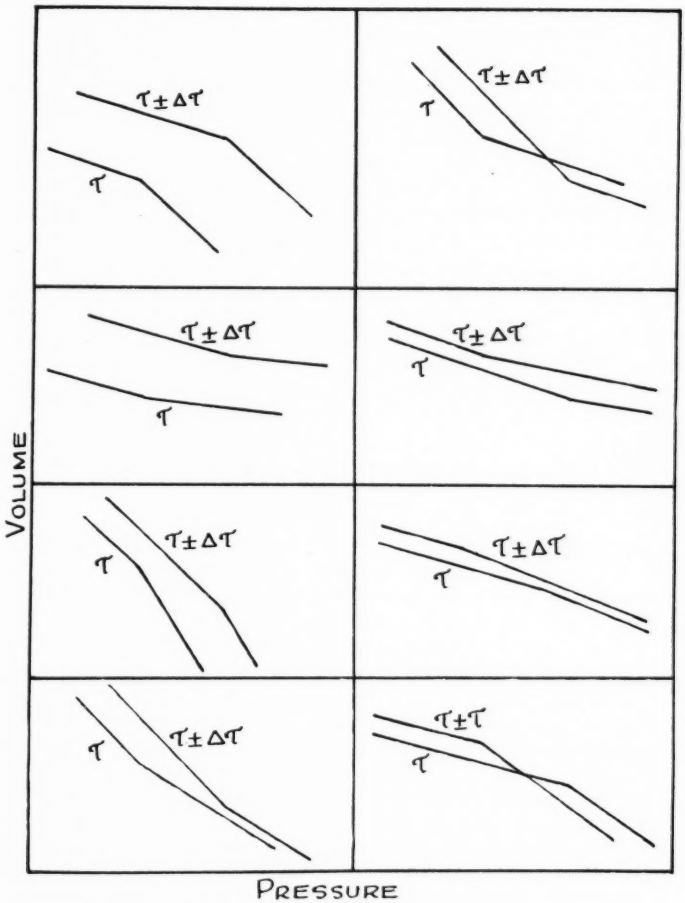

FIGURE 26. Shows the various possibilities with regard to the change with temperature of the discontinuity in the slope of an isotherm.

should not increase with increasing pressure, and such cases actually exist, although they are not very common.

The substances of this paper afford many examples of discontinuities in which the system on the high pressure side of the discontinuity has a greater compressibility than on the low pressure side. To take a single example, every other one of the breaks of the W 30%, Co 70% alloy must obviously be of this kind.

A complete thermodynamic description of the discontinuities measured in this paper would demand that the isotherms be spaced close enough to permit an evaluation of $d\tau/dp$. This evidently is not possible in most of the cases. Thus in Figure 23 for the W 30% Co 70% alloy, it is not obvious how the breaks of the 30° curve are to be made to correspond to the breaks of the 75° curve, and failing such a correspondence it is not possible to calculate $d\tau/dp$ at any of the breaks. In some cases, however, the calculation is possible. Thus the two breaks at low and high pressures respectively of the W 10% Co 90% alloy obviously correspond, so that $d\tau/dp$ can be found for both these breaks. The Ag 75% Au 25% alloy shows how the breaks may be correlated when the isotherms are closely enough spaced, although this would have been impossible otherwise. If only the 30° and the 75° isotherms were known for this alloy, the proper correlation would have been exceedingly questionable, but with the aid of the 50° isotherm there cannot be much doubt. Thus, the break at 1900 kg. at 75° has been displaced to 560 at 50°, and at 30° had dropped out to negative pressures. Similarly the 3000 point at 75° is displaced to 1200 at 50°, and is also out of the picture at 30°. The 9100 break at 75° moves to 7100 at 50° and to 4900 at 30°. The 9600 break at 75° goes to 7700 at 50° and 6900 at 30°. The two breaks at the highest pressures at 30°, 10000 and 10700, are presumably displaced to pressures higher than 12000 at 50° and 75° and so could not be detected. These two examples show the possibility of either sign for $d\tau/dp$; it is negative for the two breaks of the W 10% Co 90% alloy, and positive for all the breaks of the Ag-Au alloy.

With regard to the numerical values of $d\tau/dp$ there seems no reason to anticipate that any sort of restriction will hold. It is known that there is no restriction on the $d\tau/dp$ of possible transitions from one solid phase to another. The mechanism of the discontinuity in the derivative is doubtless more complicated in many cases than the mechanism of a phase change, and it would be most surprising if as wide a range of variation of relations between the various parameters were not possible.

The most interesting question to be answered in connection with these discontinuities is what the mechanism may be which is responsible. The most important clue is doubtless the fundamental fact that we are not concerned here with discontinuities in the volume, but with discontinuities in the derivatives. This means that whatever internal change is responsible is spread over a range of pressure and temperature, instead of being abrupt, as in an ordinary polymorphic transition or phase change of a pure substance. This means that changes in the type of lattice structure may be ruled out as the explanation of these discontinuities. Direct experimental proof has been given by X-ray analysis that no change of lattice structure occurs during the anomalous volume changes of NH_4Cl.

Phase changes in impure substances, when the impurity is not equally soluble in the two phases, are spread over a range instead of being abrupt. However, phase changes in the presence of impurity are accompanied by hysteresis effects, due to diffusion of the impurity from one phase to the other, and such hysteresis effects are absent from many of the discontinuities examined above. In fact, it is one of the most striking characteristics of most of these phenomena that they are free from hysteresis. The only exception is the Fe-W alloys, which all show hysteresis.

The existence of phenomena of hysteresis are not difficult to understand in alloys where the phenomena of solid solubility are met, for we have the possibility of the limits of solubility being altered by pressure, and so internal changes being initiated by changes of pressure. It is doubtful, however, whether anything as simple as this can explain the pressure effects, even in the Fe-W alloys. The phase diagram for Fe-W as given by Sykes[13] indicates that the region between 10 and 30% W is a two phase region, the alloy breaking up into a mixture of WFe_2 and a solid solution of about 8% W in αFe. The only possibility here would seem to be a change produced by pressure in the solubility limits of the solid solution of W in αFe, but in this case alloys of different compositions should show the same sort of anomaly, the effect of changing the gross composition being merely to change the numerical magnitude of the effect because the fractional part played by the solid solution in the whole phenomenon varies as its relative amount with regard to the WFe_2 varies. As a matter of fact, the pressure effects on the 10%, 20%, and 30% alloys are quite different in character. This suggests that the correct phase diagram of W-Fe is much more complicated than at present known, and that there must be many small scale effects not yet found

in the region now supposed to be occupied only by mechanical mixtures. This also suggests the possibility of a pressure exploration as a tool in detecting in alloys small scale structure not at present detectible by other methods.

For those substances which do not show hysteresis the conclusion would seem to be justified that the mechanism responsible for the discontinuity must be some intimate affair of the structure elements, and cannot be anything like those changes of lattice type that involve tearing down and building up again the lattice structure with comparatively large motions of some of the elements of the lattice or like anything else that involves motion of the elements of the structure through large distances. There are, of course, types of lattice rearrangement in which only a very slight change of position of some of the elements is demanded, as for example, in the inversion of quartz, which is accomplished by a slight angular displacement of each of the oxygens. But even such a change of lattice type would not satisfy our requirements, because it is accompanied by a discontinuity in the volume instead of in the derivative. Doubtless the explanation of Pauling[14] for the anomalies of NH_4Cl exemplifies the sort of thing involved. It is supposed that at a certain temperature the NH_4 radicals begin to acquire rotational motion, instead of the oscillational motion with which they are content at low temperatures, and that above a certain temperature practically all have acquired this rotation. This sort of thing cannot be general, however, but must be regarded only as suggesting one type of thing that might happen. For example, RbCl, described in another paper, has a break which cannot well be due to this sort of thing, because of the spherical symmetry of the ions. It would seem that the anomaly of RbCl must demand some internal change in the ions themselves, such perhaps as a change in the size of one of the electron shells. When one considers that the accurate solution of the wave mechanics problem demands that the wave equation be set up for the whole complicated system with every particle reacting on every other, and that the system cannot be regarded as built up of rigid building blocks, one sees enormous possibilities for small scale complications.

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